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by

Frank James Preston, B. Sc. (Hons., Glas.)

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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CONTENTS

SUMMARY

The mass spectra of complexes derived from reactions of substituted azobenzenes, benzophenoneazines, phenyl hydrazones and benzalanilines with iron carbonyls are discussed and structures proposed. The ability of iron carbonyls to cleave nitrogen - nitrogen bonds and, in some cases, to produce molecular rearrangements within aromatic nitrogen systems is demonstrated. Deuterium labelling at chosen sites within the complexes derived from substituted benzalanilines has elucidated the mechanism of formation and the position from which the hydrogen atom, which is transferred, originates. Discussion is also made on the effect of substitution upon the mass spectral decomposition of these complexes.

In other sections the electron impact induced dissociation of cyclopentadienyl μ-mercaptido, μ - alkoxo and μ dialkyl amido binuclear metal complexes of chromium, iron and nickel are compared according to the effect of the ligand system and the metal atom involved and arguments are proposed which take account of σ and π donor and acceptor abilities of the ligands. Deuterium labelling studies are also included to differentiate sites of hydrogen transfer in elimination of cyclopentadiene, benzene and mercaptans from these systems. The formation of the corresponding metallocenes under electron impact

is also deliberated upon and effects of the ligand system upon its formation taken into consideration.

Finally rearrangement ions occurring in the mass spectra of some polyfunctional cyclopropane systems are compared with known rearrangement processes in related aliphatic compounds and the differences noted are discussed in terms of structure and ion stabilities. In addition rearrangement processes having no precedent in related aliphatic compounds are discussed.

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CHAPTER ONE

INTRODUCTION

A mass spectrometer is an instrument designed to produce a beam of ions, which are separated according their mass to charge ratios, so as to form a spectrum in which the relative abundance of each species present can be measured.

Although the beginnings of mass spectroscopy can be traced back to 1886 when Goldstein discovered "canal rays", the first apparatus which allowed a study and separation of positive ion beams was constructed by J.J. Thomson in 1910 (1). The spectrum obtained from this first mass spectroscope which was recorded on a photographic plate, was a series of parabolic curves, each curve corresponding to an ion species of a particular mass/charge ratio, and it was with this instrument that Thomson gave the first direct experimental evidence that stable elements consisted of a number of isotopes of different masses.

The next major advance in instrumentation took place in 1918 when Aston (2) and Dempster (3) independently completed their first mass spectroscopes. Aston's instrument was an improvement over Thomson's in that ions of the same

mass/charge ratio were refocused along a short straight line image, regardless of their initial energies, i.e. it possessed the property of velocity focusing. This instrument, which had a resolution of 130, was used by Aston to study the isotopic constitution of a large number of chemical elements.

Dempster's instrument did not possess the property of velocity focusing but employed instead a principle first used by Classen in 1907 in his study of the mass/charge ratio of electrons, namely that charged particles of a given mass and energy diverging from a slit in a magnetic field cross again forming an image of this slit after deflexion through 180°. Essentially mono-energetic beams of ions were produced within the ion gun by making use of a collimating system of slits, the last of which was situated within the homogeneous magnetic field. The ions were refocused after travelling through a semi-circle, at a position along the plane containing the ion entrance slit, and at right angles to the direction of motion of the ions at this entrance slit. Dempster also introduced the use of an electrometer in order to measure the intensity of the ion

currents with greater precision than could be achieved with a photoplate, and thus made the instrument more suitable for the measurement of isotopic abundances than for accurate mass determination. The Dempster instrument, possessing angular or direction focusing properties was the first of a large series of so-called 'single focusing' mass spectrometers.

The focusing properties of mass spectrometers can be summarized as follows. Velocity focusing is the focusing of a beam of ions, homogeneous in mass, moving in the same initial direction at different speeds, while angular or direction focusing is the focusing of a beam of ions, homogenous in mass moving at the same speed but with different initial directions. Aston's spectrograph and Dempster's spectrometer, had only single-focusing properties, the former having velocity, but not angular focusing; the latter had angular, but not velocity focusing of the ion beam.

Instruments possessing the properties of both velocity and angular focusing are said to be double focusing, the theory of which was first developed by Herzog (4). Modern double focusing instruments, based on the designs of Matauch and Herzog (5) and Johnson-

Nier (6), ensure, by a suitable combination of electrostatic and magnetic field selectors, that the position of the final image is independent of both angular and velocity divergence of the ions emerging from the source. With such instruments, very high resolving powers can be obtained by the use of very narrow slits, but at the sacrifice of sensitivity.

Most of the mass spectrometers that have been constructed to study the mass spectra of organic compounds utilise the Nier (7) electron bombardment source which gives a degree of velocity selection within the ion gun itself, and is therefore suitable for use in angular focusing instruments. These need not necessarily be of the Dempster design which is a particular case of the focusing action of any wedge-shaped magnetic field, and may utilise a sector magnetic field (8).

Ionization of organic compounds can also be effected by photon impact (9), field ionization (10, 11, 12) and high voltage spark (13). In general the spectra produced by each of these methods differs in nature from the others, but being consistent within themselves,

all are useful techniques within the limits of their application. In addition, the actual separation of ion beams has been accomplished by use of:-

(a) radio frequency fields as in Bennett-Redhead instruments (14), the mass synchrometer (15), the omegatron (16), the farvitron (17), and the quadrupole mass spectrometer (18).

(b) time of flight of the ions (19).

Before the 2nd World War, construction of mass spectrometers was limited to a few research groups and, although Thomson had realised the potentialities of mass spectrometry in chemical analysis, the "home made" nature of most mass spectrometers hindered their adoption for this purpose. However, the need for reliable methods of analysis of petroleum fractions and the advances in electronics design, after the 2nd World War, re-awakened interest in the mass spectrometer as an analytical tool. Analytical methods (20, 21) were devised which relied on three criteria:-

(i) the mass spectrum of a given compound is fairly reproducible under fixed operating conditions.

(ii) the mass spectrum of a mixture is a linear combination of the mass spectra of the components of the mixture.

(iii) the ion abundance of a chosen reference peak of a given component is directly proportional to the partial pressure of that component in the mixture.

The introduction (23) of a heated inlet system allowed the determination of the mass spectra of organic compounds of lower volatility which were stable to higher temperatures provided all metal parts were excluded from the sample inlet system. The compound to be examined is volatilized and expanded into a heated reservoir which admits the sample into the ionization chamber through a leak.

The mass spectra of involatile solid samples and thermally instable compounds still posed a serious problem and, in order to obviate this difficulty, the direct introduction of sample vapours by sublimation from a probe was developed (23). Later versions of this system, employing a vacuum lock, have the

advantage that the mass spectrum of practically every kind of organic compound can be determined rapidly with as little as 1 μ g., and are now standard attachments to most commercial instruments.

More recently the technique of coupling mass spectrometers with gas-liquid chromatographic separation (24) has allowed the separation and identification of many component mixtures. The pressure difficulties encountered in earlier attempts due to the large concentrations of carrier gas have now been largely eliminated by the development of "molecule separators" by Ryhage (25) and Biemann (26).

As more and more data was collected on the so-called mass spectral cracking patterns of molecules, it became obvious that a basic theory of ion decomposition was necessary. Two diverse approaches to the subject were made. The mathematical approach of the quasi-equilibrium theory (27) rests on some basic assumptions regarding the ionization of molecules by electron bombardment. In the case where

the interatomic distance is the same for the molecular ion and the neutral molecule then the appearance potential will be the same as the ionization potential, i.e. this is a vertical Franck-Condon transition. In the polyatomic ion, however, it is assumed that any excess energy imparted to the molecule has sufficient time to be distributed as vibrational energy over the whole molecule, but that if many vibrational modes are excited or a few are excited to high quantum numbers dissociation can occur in those bonds with high vibrational quanta. This dissociation process is considered as a series of competing, consecutive, unimolecular reactions which can be calculated by an appropriate form of the absolute rate theory.

Before the actual theory can be applied to specific cases, complete information on all the decomposition processes from the parent ion together with experimental measurement of the activation energies and energy transfer functions of these processes must be known. Using certain refinements, such as in the case of Morrison's measurements (28) of the second derivative of the total ionization as a function of electron energy,

information can be gleaned regarding the distribution of energy transferred by electron impact. A precise estimate of these energy distribution functions marks a major step in providing one of the critical pieces of information required for the totalcalculation of the mass spectra.

In conclusion, it may be said that the theory postulates a certain form for rate equations, devises a certain reaction sequence, inserts values of parameters like the activation energy, frequency factors etc., and finally, using the proper energy distribution function, enables the calculation of the mass spectrum of a molecule. In spite of the difficulties involved, such calculations have been made for small molecules, which agree reasonably well with the experimental values. The problems encountered, however, in application to larger molecules have precluded calculations in the bulk of organic compounds. Critical assessments of the future of the theory have been made (29, 30).

The other main approach relies on the consideration of the ionized molecule in the same light as organic solution chemistry, i.e. in terms of concepts

such as resonance; inductive effects; stabilities of carbonium, oxonium ions, transition states, etc. McLafferty has postulated that the factors which determine the formation of abundant ions in mass spectra are the relative stabilities of:-

(i) the ion and neutral fragment.

(ii) the bonds of the decomposing ion.

(iii) the possibility of fragmentation through a cyclic transition state (31). The same author has also demonstrated mass spectral features related to known "solution effects", in the quantitative relationship of ion abundances of substituted benzoyl compounds to the Hammett "sigma" constants of these substituents (32). Successful application (33) of this relationship has been made in the estimation of competing processes in retro-Diels Alder dissociations of organic ions in the mass spectrometer. Arguing almost entirely from thermochemical data, Macoll (34) has also equated the behaviour of carbonium ions in solution and in the mass spectrometer. Such evidence lends more weight to the theory that mass spectral reactions parallel those of solution chemistry.

The theory, however, requires that the charge

be localized at favoured positions in the molecule, normally on hetero-atoms or other functional groups, by removal of an electron from a non-bonded lone pair. Measurement of the ionization potentials of ketones (35) parallel fairly well the estimated energy of the non-bonded pairs on oxygen, and must lend some weight to the idea. However, deficiences in the localized charge concept have been pointed out (36) and have limited its acceptance by many workers.

Biemann (37), using a physical-organic approach without the localized charge theory, has given a set of empirical rules, which attempt to summarize known fragmentation processes.

One of the schools which has made extensive use of the localized charge concept, or rather its development in the radical-ion concept (38), is that of Djerassi and his associates (39). As an aid to the understanding of mass spectrometry processes, the same group has, by the use of compounds suitably labelled with heavy isotopes, elucidated the mechanisms of many hydrogen rearrangements which are often observed in the mass spectra of organic molecules. In more recent work (40)

they have tried to demonstrate the specificity or non-specificity of hydrogen migration in even and odd electron systems, and although claiming success in the majority of cases, have encountered some exceptions to their theories.

Utilizing the same kind of approach McLafferty (41) has discussed a generalized mechanism for mass spectral reactions, in which the positive charge and unpaired electron of an odd electron ion can be positioned at different sites in the ion, each exerting a separate influence on the course of fragmentation of the ion.

Within the field of mass spectrometry in its application to organometallic compounds, very little research was done before 1964. Investigations had been made on the alkyls of mercury and lead (42); the metal carbonyls of iron and nickel (43) and some organic substituted iron carbonyls (44); and several papers had been published (45) on the mass spectra of metallocene compounds. The major difficulty in dealing with organometallic compounds is their thermal instability on glass and metal surfaces, this being especially true of

the metal carbonyl complexes and it was not until the advent of the direct insertion probe that the utility of mass spectrometry in this field was realised. Since 1964, the literature has steadily increased to include π- bonded organometallics such as metallocenes and metal cyclopentadienyls (46); organometallic carbonyls and nitrosyls (47); binuclear metal complexes (48); othalocyanins and metal chelates (49).

Shannon (50) has postulated theories of ion decomposition based on the premise that the oxidation state of the metal atom should direct the fragmentation and, in later papers (48a) (49b), he has attempted to show that the even or odd electron nature of the molecular and fragment ions is inter-related with the oxidation state of the metal atom and the nature of the fragment lost.

Probably the most stimulating idea to the progress of mass spectrometry in its modern form was the realization by Beynon (51) that differences in the nuclear packing fractions of the elements (52) made it possible to distinguish ions of the same nominal mass but differing

chemical constitution, and if instruments of high enough resolving power could be built then the necessary separation in mass could be achieved. The development of this idea not only meant that the molecular formulae of compounds could be determined, but also good evidence for their structure could be obtained by accurate mass measurement of their fragment ions.

The methods of precise mass measurement depend on the geometry of the mass spectrometer. In instruments of Mattauch-Herzog geometry the high resolution spectra of the sample and of a calibration compound, normally a perfluorinated hydrocarbon, are recorded simultaneously on a photographic plate. Distances between the lines corresponding to ions of unknown constitution and those of the calibration compound can then be related to differences in mass. This technique has been extended by Biemann (52) to the automatic determination of the mass of all the ions in the spectrum and, using a suitably programmed computer, 'element maps' have been prepared in which the constitution of the ions are arranged in increasing

order of their elements. More recently this technique has been speeded up (53) at the actual ion comparison stage and complete data processing for element map preparation can be achieved in twelve minutes.

In instruments of Nier-Johnson geometry, mass measurement is effected by the "peak-matching" technique (54). The time taken to make measurements on a complete spectrum by this method is exceptionally time consuming and in normal conditions only specific "key" ions in the spectrum are determined. A system suitable for use in mass spectrometers of this design, which allows the complete spectrum of sample and calibration compound to be recorded in ten seconds at a resolution of ten thousand, has been described (55). In this system the spectra is recorded on magnetic tape in digital form and the time interval between the ions is related to the mass difference of the ions.

The obvious development from this ability to deal with mass spectra in an automated fashion has been its application to automatic structure analysis. This has been applied with considerable success to the determination of the amino acid sequence of peptides

(56, 57), where the preferred fission of CO-NH and CO-R bonds leads to a very large number of combinations of the amino acid units, and also where there are the minimum number of rearrangement ions. The computer aided correlation of metastables in high resolution mass spectrometry (58) has also made a great contribution to these analyses.

The great disadvantage, however, in the application of automatic digital methods to structural analyses lies in alkyl and phenyl migrations of ions which have been discovered recently (59) and their prediction for other structural types. As a step towards this solution Biemann (60) has adopted the idea of "ion types" for structural analysis of totally unknown compounds.

Obviously there is still room for a great deal of research into the reasons for electron impact dissociation before all the available information can be co-ordinated and maximum use made of fast, reliable data processing facilities.

CHAPTER 1

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CHAPTER 2

The Structural Elucidation of Iron Carbonyl Complexes of Organic Nitrogen Compounds.

CHAPTER TWO

THE STRUCTURAL ELUCIDATION OF IRON CARBONYL COMPLEXES OF ORGANIC NITROGEN COMPOUNDS.

INTRODUCTION

The reaction of iron carbonyls with nitrogen containing compounds has been the subject of several investigations,(1-6). For example (4), it has been demonstrated that the treatment of iron pentacarbonyl with pyrrolidine at low temperatures gives $Fe(CO)_3$ $(pyrrolidine)_2$. These are primarily substitution reactions and the part played by mass spectrometry in the structural elucidation of compounds formed by substitution and/or rearrangement reactions will be discussed. As many of these compounds were formed by photochemical reaction, a brief synopsis will be given of the photochemical reactions of metal carbonyls.

The reaction of a metal carbonyl $M(CO)_x$ or its derivative $RM(CO)_x$ (M = metal, R = ligand) with an electron donor D can lead either to the substitution of a carbonyl group by the donor D, or the metal carbonyl can undergo disproportionation to form metal carbonylates, (7-9).

i.e. $RM(CO)_x \rightleftharpoons RM(CO)_{x-1} + CO$

$RM(CO)_{x-1} + D \longrightarrow RM(CO)_{x-1}D$

or e.g. $3Mn_2(CO)_{10} + 12D \longrightarrow 2\left[MnD_6\right]\left[Mn(CO)_5\right]_2 + 10CO$

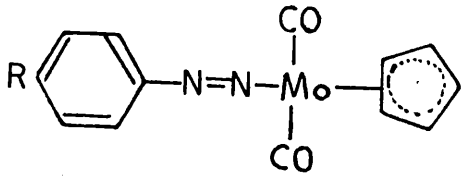
In a photochemical reaction, the unstable intermediate acceptor $RM(CO)_{x-1}$ is produced at or below room temperature on account of the high energy supplied by irradiation. This enables the isolation of products which are thermodynamically unstable with respect to further thermally induced transformation. Thus cyclopentadienyl manganese tricarbonyl does not react with triphenyl phosphine even at 200°C, but gives both mono and disubstituted products photolytically (10-11). Normally photochemical substitution occurs by an S_N1 mechanism. The process can be visualised as follows:-

$RM(CO) \xrightarrow{h\nu} \left[RM(CO)_x\right]^* \longrightarrow RM(CO)_{x-1} + CO$

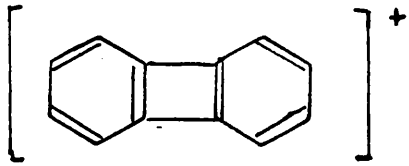
The existence of the electron acceptor as an unstable intermediate with a half-life of a few minutes has been demonstrated spectroscopically (12-15). For instance photolysis of $M(CO)_6$ compounds (M = Cr, Mo, W) at low temperatures and examination of the product by infra-red spectroscopy in the carbonyl region has demonstrated

the existence of $M(CO)_5$. It has also been argued, on this evidence, that $Mo(CO)_5$ undergoes transition from square pyramidal symmetry to that of a trigonal bipyramid at -155°C. The substitution product is then formed by the addition of a σ- or π-electron donor into the vacant orbital of the acceptor.

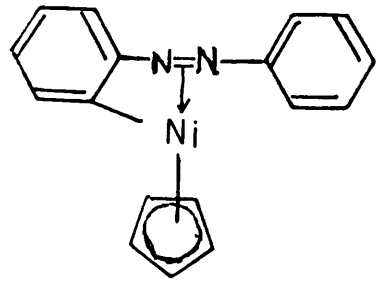
With this information in mind and the knowledge that organic compounds themselves could undergo some surprising rearrangements upon photolysis, an investigation into the possibilities of mass spectrometry as a structural tool in this field was undertaken.



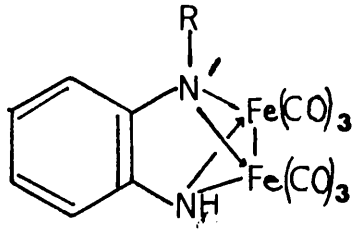
I



II



III



R=Ph

IV

Fig 1

(a) THE REACTIONS OF AZOBENZENE AND SUBSTITUTED AZOBENZENES WITH IRON CARBONYLS

When this work was begun no transition metal carbonyl complexes containing azobenzene or substituted azobenzenes had been reported, although it has since been shown that the related diazocomplexes (I) are formed from diazonium tetrafluoro-borates and cyclopentadienyl molybdenum sodium (16).

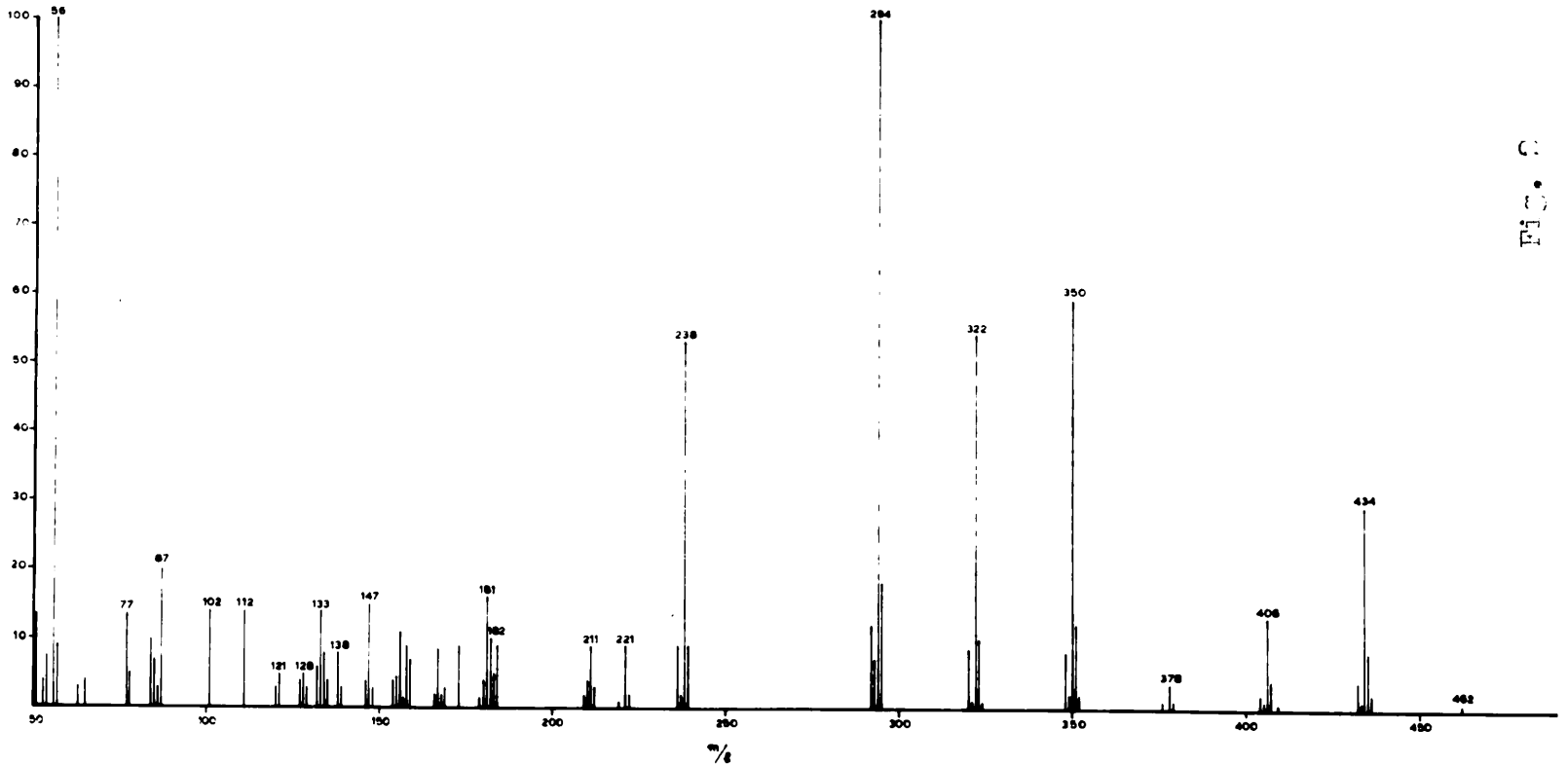
There existed a wide range of compounds of many of the transition metals having ligands attached through C = C, C ≡ C, C = O, and C = N groups, but no report had been made on the influence of metal carbonyls on azo- and diazo- compounds. As the first of a series of experiments, azobenzene and iron pentacarbonyl were irradiated in benzene. A red-brown nitrogen containing metal carbonyl complex was isolated, analysing for (azobenzene) $Fe_2(CO)_6$, which, however, was discordant with the evidence of both the infra-red and mass spectra. Absorption in the infra-red at 3362 cm^{-1} indicated an N - H stretching and although the mass spectrum showed the molecular weight to be 462 containing two irons

(isotope abundance pattern) and six carbonyls which were lost consecutively from the parent ion further fragmentation showed loss of one iron atom followed by either ammonia (to give m/e 221) or hydrogen cyanide (to give m/e 211).

These two fragmentation steps at least were enough to question an azobenzene structure as apart from the difficulty of finding suitable bonding arrangements mass spectral fragmentation of ions containing two phenyl rings linked by one or two atoms show elimination of the central atom or atoms together with two hydrogens (17), thus forming the very stable ion m/e 152 (II).

Chemical degradation of the complex with lithium aluminium hydride gave a metal-free compound containing nitrogen (i.r. N - H)with a molecular ion at m/e 184, and which precise mass measurement showed to be $C_{12}H_{12}N_2$. Additionally, fragment ions corresponding to the elimination of H, 2H, 3H, NH, NH + H, NH + 2H, and hydrogen cyanide from the parent ion were observed. Diphenylamine (17) is known to produce rearrangement ions with loss of 15, 16 and 17 mass units from the parent ion,

COMPLEX FROM AZOBENZENE



and it has also long been known that primary aromatic amines (18) eliminate hydrogen cyanide from the parent ion. This led us to believe that the degradation product was an aminodiphenylamine and indeed comparison with an authentic sample of o-aminodiphenylamine showed identical melting point, infra-red and mass spectra.

As it had been reported (19) that azobenzene could be isolated by lithium aluminium hydride reduction of the complex (III), and that no rearrangement was known involving azobenzene and lithium aluminium hydride, it was concluded that the skeleton of o-aminodiphenylamine was present in the complex.

Re-examination of the mass spectrum, together with consideration of possible bonding arrangements produced a structure (IV) which seemed to satisfy all the necessary information available.

Very strong chemical support was gained for this structure when it was shown (20) that o-aminodiphenylamine and di-iron enneacarbonyl react at room temperature in benzene yielding the same complex. Recently X-ray crystallographic studies have been made on this complex (21) which have confirmed the earlier structure.

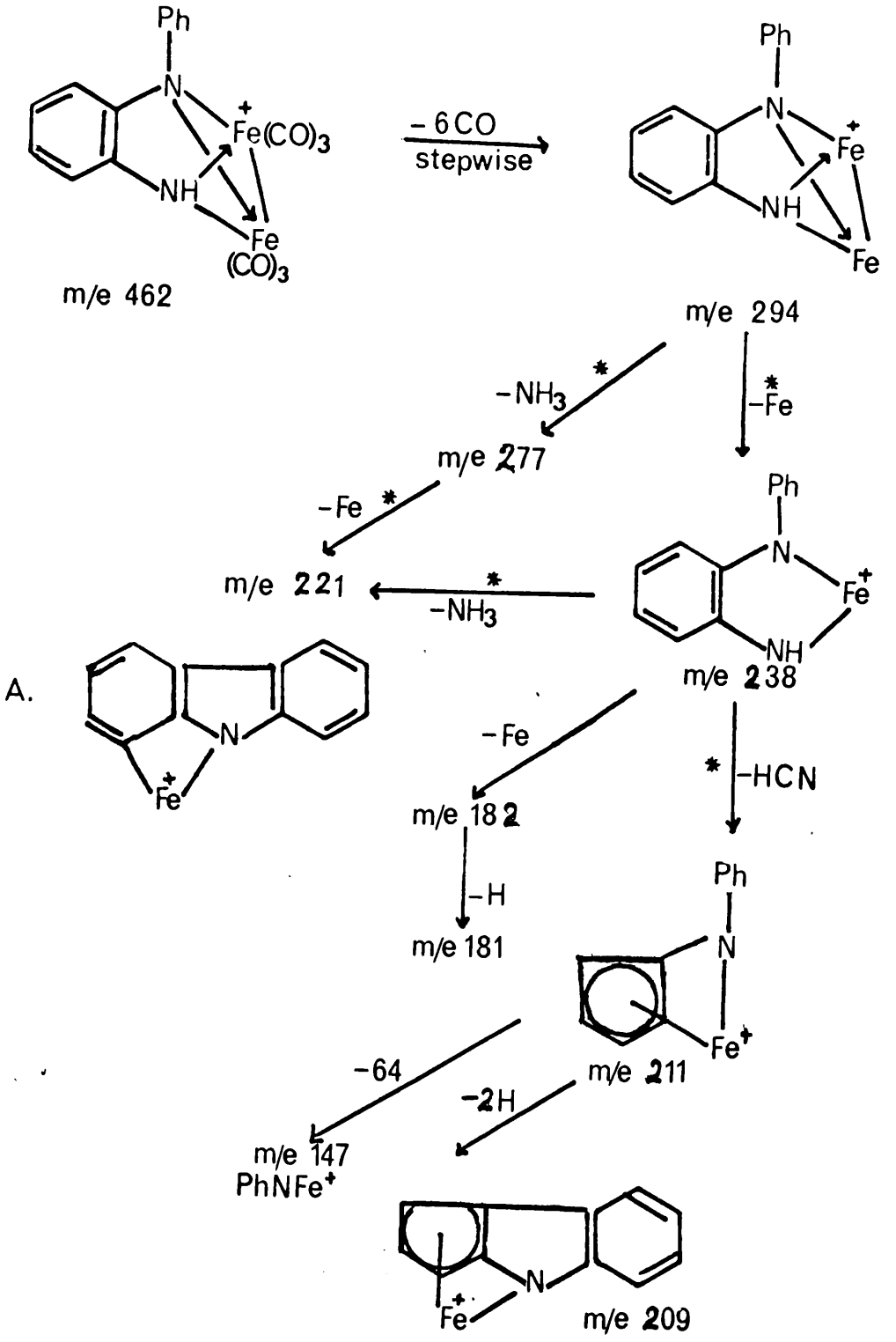

Ph
N
Fe(CO)3
NH
Fe
(CO)3
m/e 462
- 6CO
stepwise
Ph
N
Fe
NH
Fe
m/e 294
-NH3
*
m/e 277
-Fe
*
m/e 221
*
-NH3
-Fe
*
-HCN
m/e 182
-H
m/e 181
m/e 211
-64
-2H
m/e 147
PhNFe+
m/e 209
A.

Fig 3

Both nitrogen atoms bridge the two $Fe(CO)_3$ groups which are themselves arranged in an eclipsed configuration. The complete bridging group $N-C_6H_4-N$ lies perpendicular to the Fe-Fe vector (2.37Å the shortest yet reported). The central group of six atoms $C_2N_2Fe_2$ forms a bicyclo (2, 1, 1) system and a 36 electron structure can be rationalized on the supposition that each nitrogen acts as a 3 electron donor.

A more detailed account of the mass spectral fragmentation can now be given (Fig. 3). It has already been stated that all six carbonyl groups are lost consecutively from the parent ion, the base peak of the spectrum being the $(P-6CO)^+$ ion. Further fragmentation occurs by either of two possible routes as shown. Loss of hydrogen cyanide from the $(P-6CO-Fe)^+$ ion can be rationalized on the model of aniline (18) with consequent five membered ring formation and π bonding to iron. Whereas the elimination of ammonia poses some little difficulty, it can, however, be visualized to occur in a similar manner to the elimination of ammonia from the parent ion of diphenylamine (17), except that in this case it is probable that the other nitrogen atom is involved and

that the carbazole type ligand is doubly bonded to iron as in A.

m/e 221 (A) can be formed by either of the two decomposition processes shown; that via m/e 238 being the main pathway as borne out by the abundances of metastable ions for these transitions. Additional evidence for o-π type ions like m/e 211 and the formation of a cyclopentadienyl ring is to be found at m/e 121 which is attributed to the cyclopentadienyl iron ion. Support for the decompositions shown was gained from use of metastable ions and by precise mass measurement wherever necessary. Details of these measurements are given in Table 1.

Table 1

m/e	Observed Mass	Formulation	Theoretical Value	Error
294	293.93643	$C_{12}H_{10}N_2Fe_2$	293.93678	-0.0003
238	238.01932	$C_{12}H_{10}N_2Fe_2$	238.01852	+0.0008
221	220.99277	$C_{12}H_7NFe$	220.99192	+0.00085
211	211.00842	$C_{11}H_9NFe$	211.00743	+0.0010
147	146.976960	C_6H_5NFe	146.97712	-0.0008

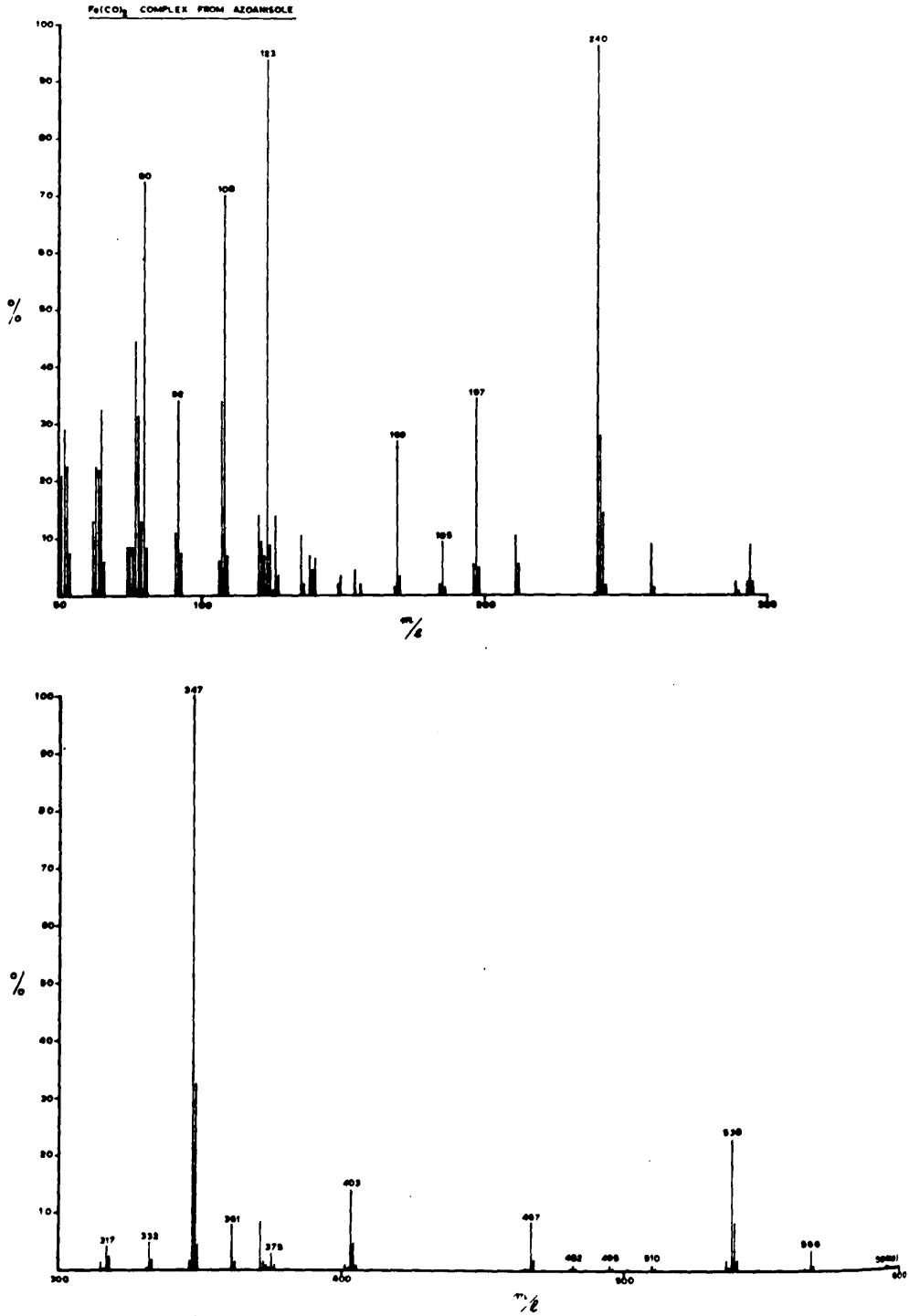
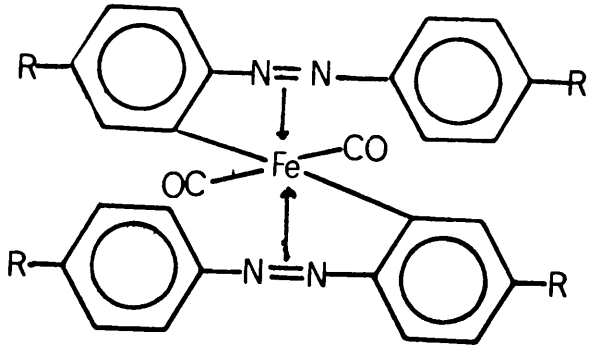

Fe(CO)3 COMPLEX FROM AZOANISOLE
%
m/e
347
240
183
90
108
92
198
197
105
%
m/e
347
403
467
336
361
317
333
279
910
300
400
500
600

Fig. 4

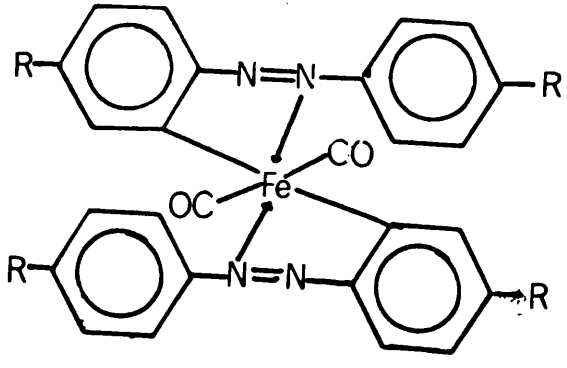
This study was next extended to include 4, 4' - disubstituted azobenzenes. 4, 4' - Dimethoxy azobenzene furnished two metal carbonyl compounds. One complex was analogous to that obtained from azobenzene as it followed the same characteristic fragmentation pattern; the other complex did not show any NH absorption in the infra-red and showed only two fundamental absorption bands in the metal carbonyl stretching region.

Mass spectrometry (Fig. 4) gave a molecular ion at m/e 594, and from the isotope abundance pattern of the parent ions, it was deduced that only one iron atom was present. Mass measurements proved the ions m/e 566 and 538 to be formed by losses of carbonyl groups from the molecular ion, and that the molecular formula was in fact $C_{30}H_{26}N_4O_6Fe$.

The ion m/e 538 (determined as $C_{28}H_{26}FeN_4O_4$) decomposed by two routes; one by elimination of an iron atom to give m/e 482 (determined as $C_{28}H_{26}N_4O_4$) and supported by a metastable ion at m/e 413.8, the other by elimination of a nitrogen molecule to produce the ion m/e 510 (determined as $C_{28}H_{26}FeN_2O_4$). The latter process was remarkably like the fragmentation processes of



V



VI

Fig 5

substituted azobenzenes themselves and suggested that a dimethoxyazobenzene residue or residues might be present in the complex. It was further argued that the step involving elimination of iron to give m/e 482 could be the removal of an iron atom from two dimethoxyazobenzene skeletons, which were attached to it by σ bonds, together with consecutive condensation between the dimethoxyazobenzene radicals formed. This was thought more likely than the existence of a dimerised dimethoxyazobenzene form within the complex, as m/e 482 represented a very small ion in the spectrum compared with m/e 240 and 241.

From a consideration of these and other ions in the mass spectrum, it was concluded that the complex might have one of the two structures. V or VI (R = OMe).

The ultraviolet spectra of 4, 4' dimethoxyazobenzene and the complex are so similar as to suggest that VI(a) is the more probable, since participation of the π electrons of the azo groups in delocalized bonding with the iron would tend to change the absorption frequencies of the system, more than would the participation of the lone pair of electrons on nitrogen.

The flow sheet opposite (Fig. 6) shows the major route of the mass spectral fragmentation of the

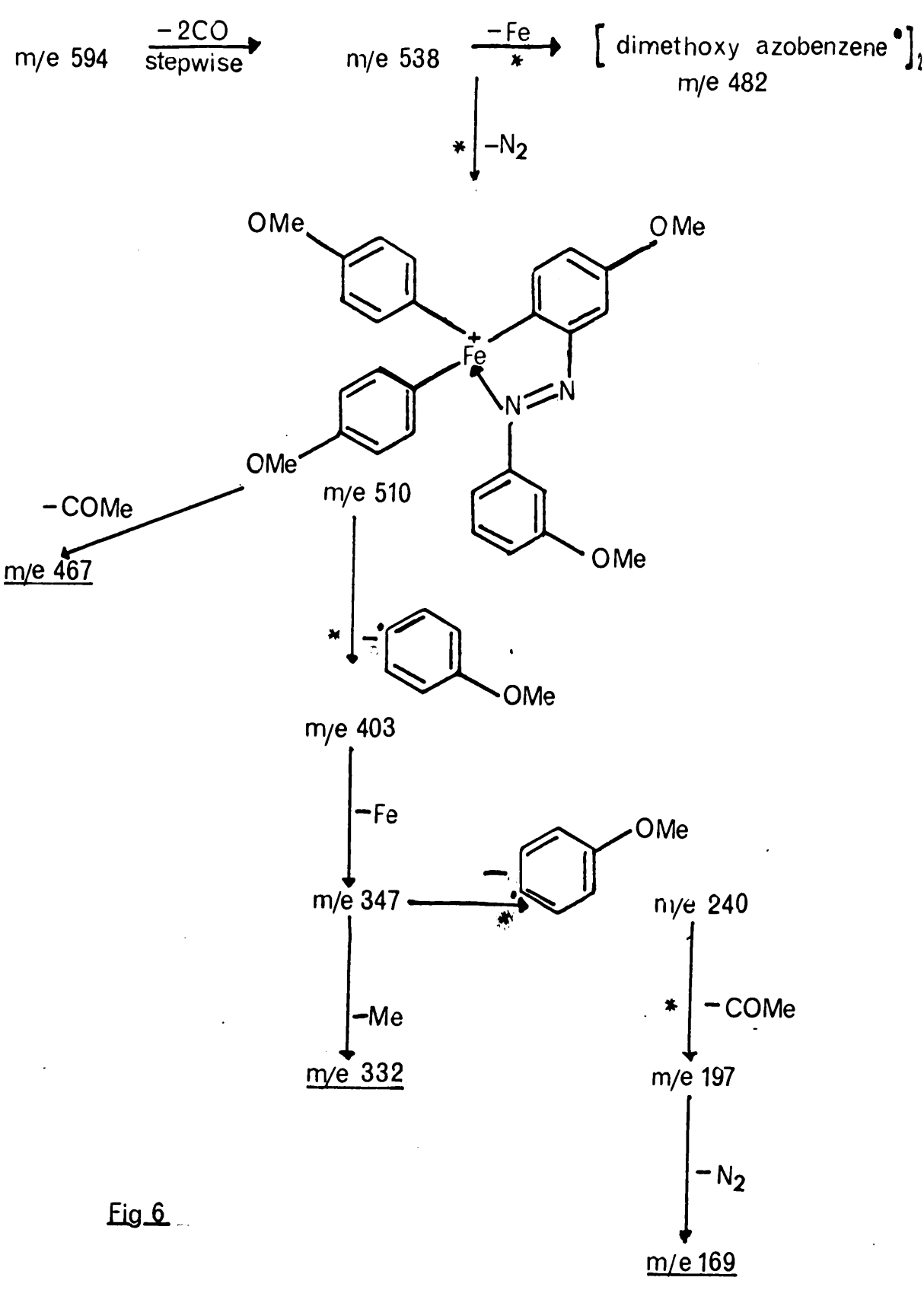

m/e 594
−2CO
stepwise
m/e 538
−Fe
*
[dimethoxy azobenzene•]1
m/e 482
* −N2
OMe
OMe
Fe
N=N
OMe
OMe
m/e 510
−COMe
m/e 467
*
OMe
m/e 403
−Fe
OMe
m/e 347
m/e 240
−Me
m/e 332
* −COMe
m/e 197
−N2
m/e 169

Fig 6

complex. It is worthwhile noting here that unlike the corresponding non-metallic ions, elimination of a nitrogen molecule from m/e 538 is not followed by loss of two hydrogens (17) to form a completely cyclic system. This can be interpreted as the formation either of a bond between the two rings on either side of the eliminated nitrogens, or of the two radical centres formed in the elimination forming bonds to iron as in m/e 510. Further, elimination firstly of C_6H_4OMe, Fe, and then again C_6H_4OMe seems to support the latter idea, the diradical m/e 240 cyclising to form a completely stable aromatic ion. A table of mass measurements made to determine the constitution of ions in the spectrum is shown below.

TABLE 2

m/e	Observed Mass	Formulation	Theoretical Value	Error
566	566.12584	$C_{29}H_{26}FeN_4O_5$	566.125237	+0.00061
538	538.13053	$C_{28}H_{26}FeN_4O_4$	538.130327	+0.0002
510	510.12420	$C_{28}H_{26}FeN_2O_4$	510.12418	-
482	482.19542	$C_{28}H_{26}N_4O_4$	482.19539	-
467	467.1021	$C_{26}H_{23}FeN_2O_3$	467.1028	-0.0007
403	403.0749	$C_{21}H_{19}N_2O_3Fe$	403.0745	+0.0004
347	347.13956	$C_{21}H_{19}N_2O_3$	347.13956	-
240	240.0909	$C_{14}H_{12}N_2O_2$	240.08987	+0.0011
197	197.07117	$C_{12}H_9N_2O$	197.0714	+0.0003
169	169.0653	$C_{12}H_9O$	169.0653	-

4, 4′ Dimethylazobenzene and iron pentacarbonyl on irradiation gave two complexes both analogous to those obtained from 4, 4′ dimethoxyazobenzene and structures V and VI (R = Me) are proposed.

It is worthwhile noting here that the rearrangement of azobenzene to o- semidene does not necessarily take place specifically under irradiation conditions, but rather it is considered that the presence of iron carbonyls is necessary to act as a reducing agent, the actual "semidene" rearrangement being accelerated by the ultra violet radiation. It has in fact been shown (22) that nitrosobenzene and azobenzene both react with di-iron enneacarbonyl under thermal conditions to give the complex IV in extremely low yield.

As is confirmed by the X-ray structure determination (21) no bonding occurs between the phenyl ring and iron, all bonding being considered to take place through three electron donation from the nitrogens. It was, therefore, not surprising that the reaction of iron pentacarbonyl with o-phenylene diamine (20) produced a complex which we considered to be of the same basic

General Fragmentation Pattern for N Substituted o-Phenylenediamine Complexes

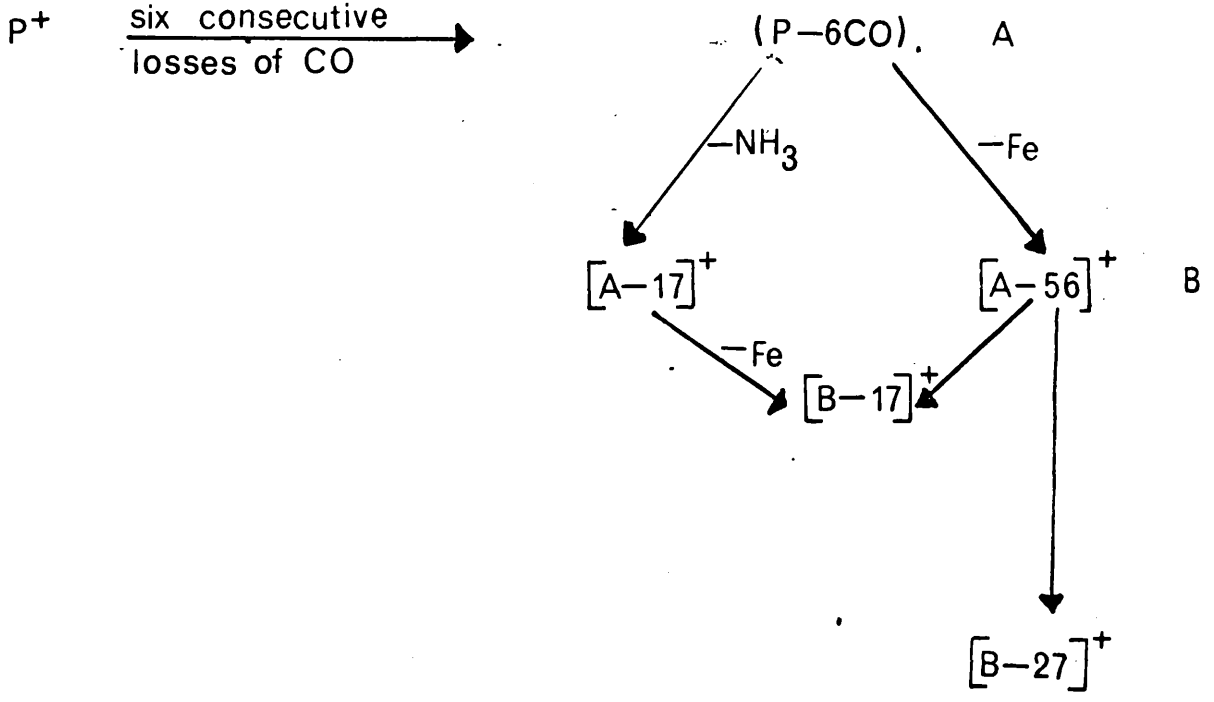


Fig 7

structure as IV with R = H.

The mass spectrum of this complex follows the same fragmentation pattern as that observed for the other diphenylamine complexes, the main features of which can be seen in Fig. 7. However, further fragmentation obviously depends on the nature of substitution on N'.

As yet, no certain mechanism is known whereby the azobenzene nucleus is first of all reduced then rearranged to its final form. Reactions are known where certain cyclic hydrocarbons (23) are rearranged to bicyclic systems, e.g. cyclohexa-1,4 diene rearranges on the surface of iron carbonyl to give cyclohexa - 1, 3 - diene. These reactions seem to parallel certain features of acid catalysed rearrangement, and in this sense the rearrangement of azobenzene to o- semidene on the surface of iron carbonyls is similar to the acid catalysed rearrangement. The usual course of this reaction, the transformation of hydrazobenzenes to derivatives of 4, 4' - diaminobiphenyl, tends to predominate with ortho - and meta - substituted hydrazobenzenes and may also occur with certain para-substituted hydrazobenzenes if the para

substituent is readily subject to electrophilic displacement. More generally, however, para substituents divert the rearrangement into one or more alternate courses. Hydrazobenzenes having para substituents on both rings are commonly transformed to derivatives of 2 aminodiphenylamine (ortho-semidenes); whereas hydrazobenzenes with single para substituents may be converted to derivatives of 2, 4' diaminobiphenyl (diphenylenes), to para semidenes, or to mixtures of these products. Obviously any mechanism proposed for the benzidene rearrangements must account for formation of each of these products.

The rearrangements of hydrazobenzenes to benzidines (24, 25, 26) to diphenylenes (27) and to o-semidenes (28) are third-order reactions; first order in substrate and second order in hydrogen ion. The rearrangements are subject to specific hydronium ion, rather than general acid catalysis and proceed more rapidly in D_2O than in H_2O, (28). It, therefore, appears likely that the rate-determining step involves only the "double conjugate acid" of the substrate - that is the cation $(Ar - NH_2 - NH_2 - Ar)^{2+}$. It has also been found that para - deuterated hydrozobenzene undergoes

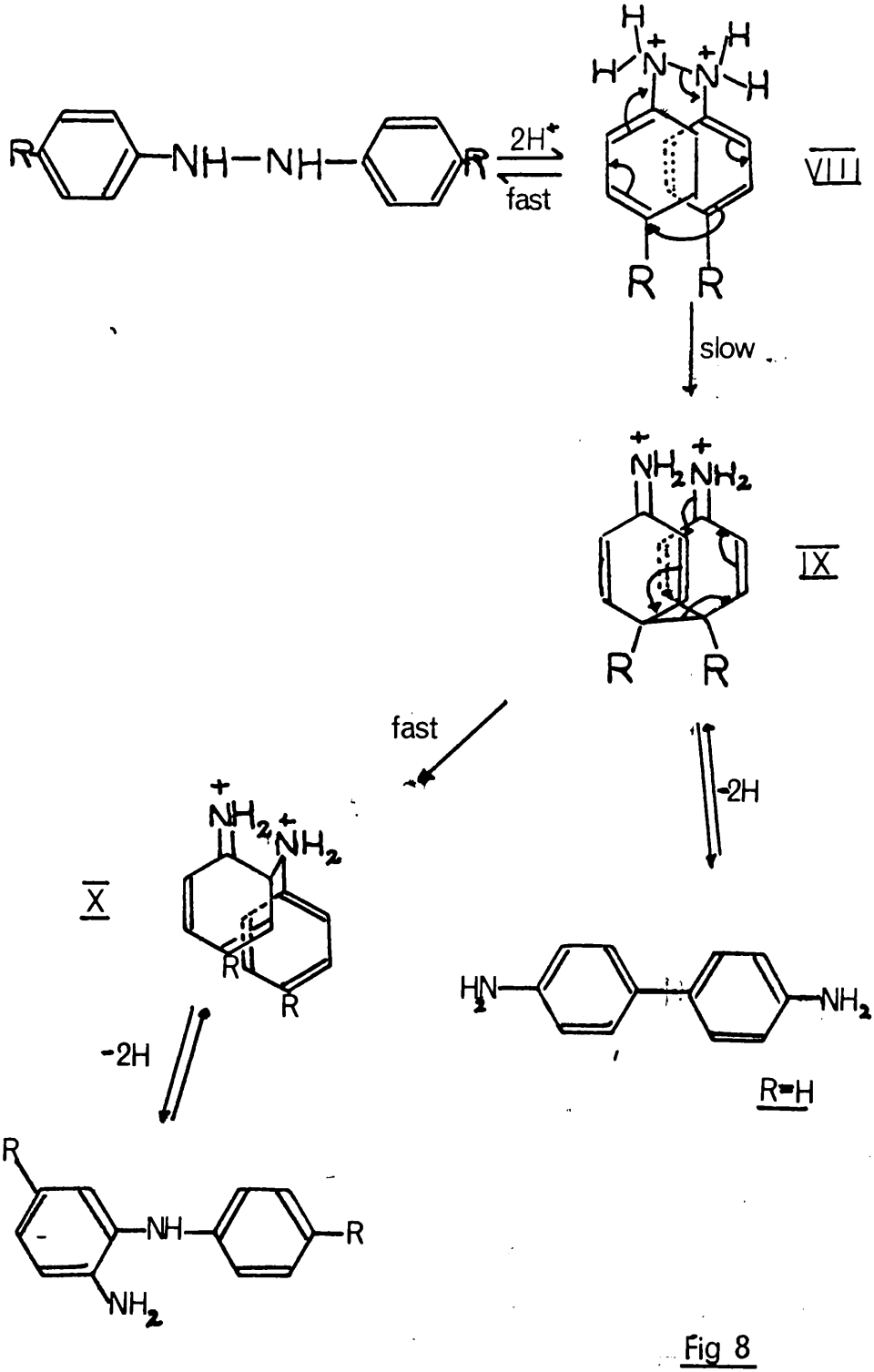
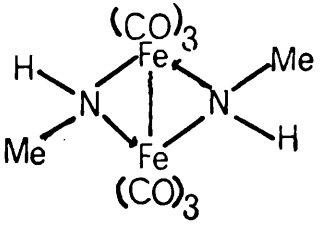

R
NH
NH
R
2H+
fast
VIII
R
R
slow
IX
R
R
fast
-2H
X
R
R
-2H
HN2
NH2
R=H
R
NH
R
NH2

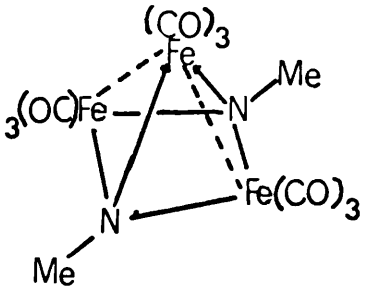
Fig 8

the benzidene rearrangement at very nearly the same rate as does non-deuterated hydrazobenzene (29) suggesting that the para-hydrogens become detached from the ring after, rather than during, the rate determing step. The available data on the benzidene and o-semidene rearrangements then points to the cyclic mechanism shown opposite, Fig. 8. Here it may be assumed that the easy cleavage of the N-N bond is largely due to the electrostatic repulsion between the two positively charged nitrogen atoms.

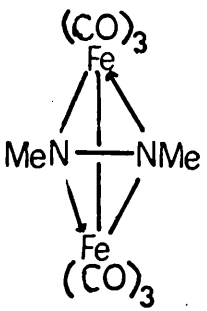
It is not suggested that the iron carbonyl catalysed reaction necessarily follows that of acid catalysis: nevertheless it may be possible that hydrogenation and protonolysis of azobenzene may take place on the surface of the metal carbonyl to form o-semidene via VIII → X. o-Semidene will then react with iron enneacarbonyl in solution to give the complex IV. It may well be that protonolysis is not necessary and that the rearrangement to o-semidene occurs by the formation of a transition state involving a metal-arene π-complex.



XI



XII



XIII

Fig 9

It is relevent here to note that the reaction of nitromethane with di-iron enneacarbonyl yields two products XI and XII (Fig. 9), and it is thought that the reaction may proceed via azomethane and hydrazomethane by a mechanism similar to that of azobenzene without the possibility of nitrogen to carbon migration. Structures were proposed on the basis of the mass spectral evidence, the main features of which are shown in Figures 10 and 11. Compound XII is analogous to the compound $S_2Fe_3(CO)_9$ (30), formed in the reaction between 2-mercaptobenzo-thiazole and tri-iron duodecacarbonyl, the sulphur positions being replaced by NMe groups. It would then be expected that the related di-iron complex would exist as XIII having analogies with both $S_2Fe_2(CO)_6$ and $(N_2H_2)Fe_2(CO)_6$ (31, 32). The molecular weight of 340, however, requires an additional two hydrogens, one on each nitrogen, and hence the structure XI is proposed for this compound. As the mass spectra are quite straightforward, discussion will be limited to the visual representation of the cracking patterns in figures 10 and 11. The important deduction to be made from this observation is the ability of metal carbonyl surfaces to reduce and cleave nitrogen-

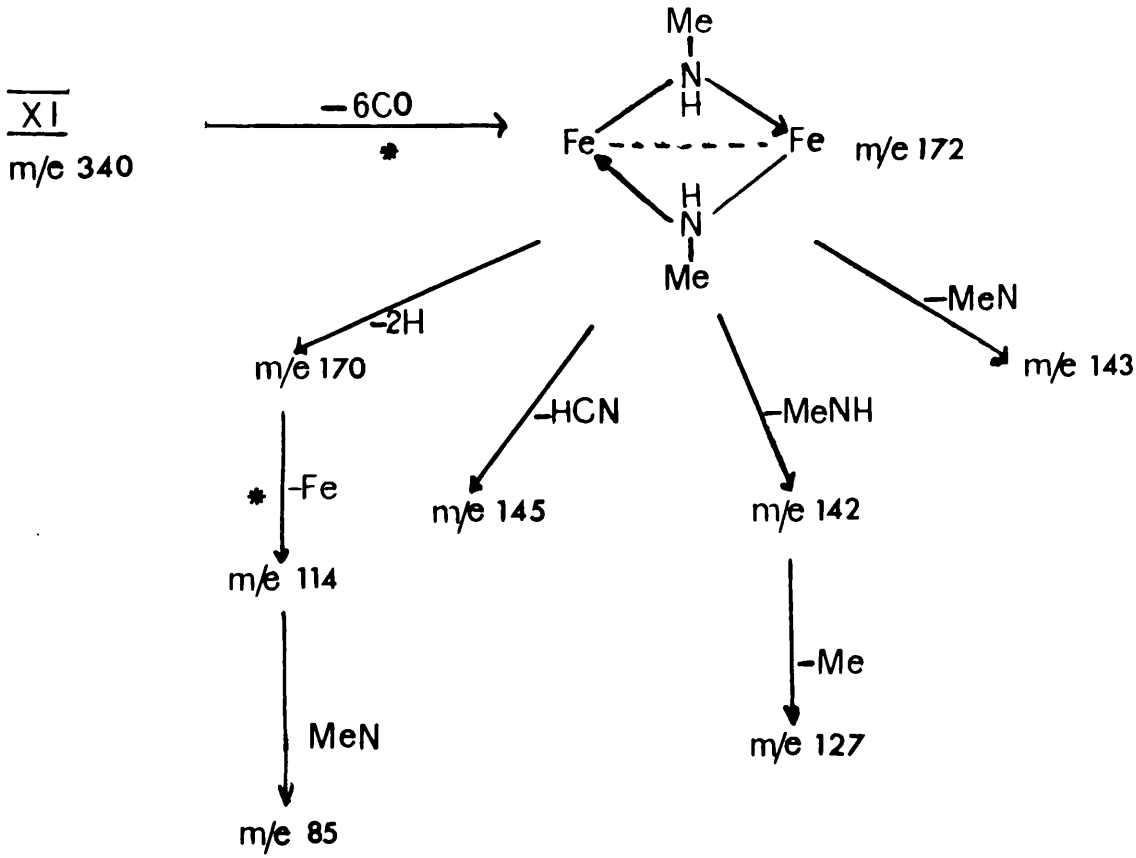

XI
m/e 340
−6CO
*
Me
N
H
Fe
Fe
m/e 172
H
N
Me
−2H
m/e 170
−HCN
m/e 145
−MeNH
m/e 142
−MeN
m/e 143
* −Fe
m/e 114
MeN
m/e 85
−Me
m/e 127

Fig. 10

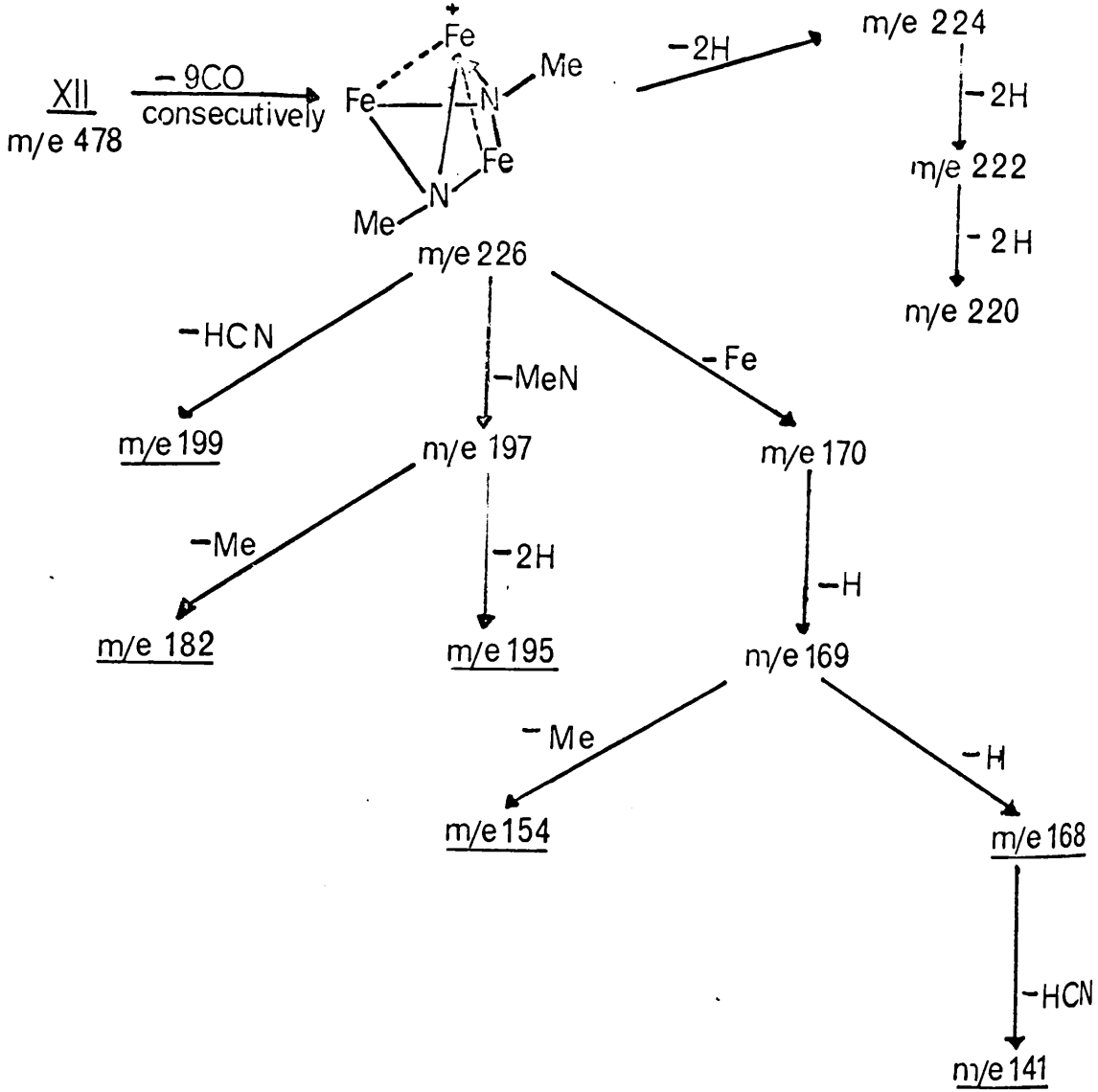

XII
m/e 478
−9CO
consecutively
Fe
Me
N
Fe
N
Me
−2H
m/e 224
−2H
m/e 222
−2H
m/e 220
m/e 226
−HCN
m/e 199
−MeN
m/e 197
−Fe
m/e 170
−Me
m/e 182
−2H
m/e 195
−H
m/e 169
−Me
m/e 154
−H
m/e 168
−HCN
m/e 141

Fig 11

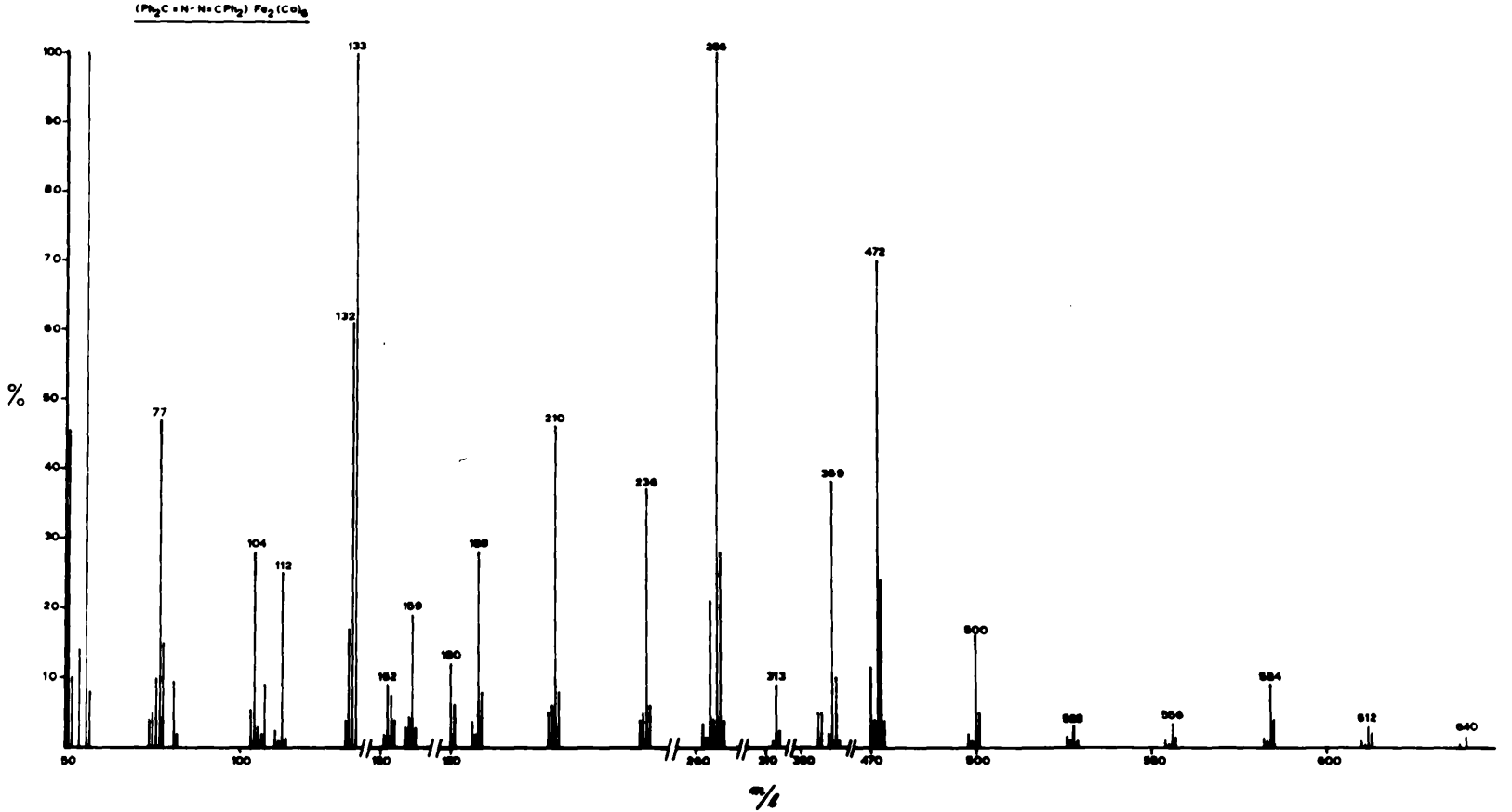
nitrogen bonds to form one or several products with which they themselves react yielding stable products.

A later discussion on the formation of complexes involving the cleavage of nitrogen - nitrogen bonds in azines and phenyl hydrazones, will show the generality of a reaction the mechanism of which is yet unknown and which poses a problem of considerable chemical interest.

(b) Reaction of Azines with Iron Carbonyls

In the course of a related investigation it was found that benzophenone azine had been formed during the irradiation of diphenyl diazomethane and iron pentacarbonyl, and investigations were carried out on the reactivity of this azine with iron carbonyls. No complex, however, was formed by irradiation of benzophenoneazine in the presence of iron pentacarbonyl, whereas the reaction carried out with di-iron enneacarbonyl in benzene under reflux yielded a stable orange complex which analysed as (benzophenoneazine) $Fe_2(CO)_6$.

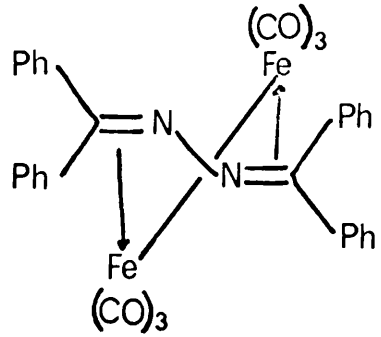
The mass spectrum showed a parent molecular ion at m/e 640 (^{56}Fe) and a precise mass measurement of the


(Ph2C=N-N=CPh2) Fe2 (Co)6
%
m/e
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
350
400
450
500
550
600
77
104
112
133
132
152
169
180
188
210
236
286
313
389
472
500
528
556
584
612
640

$(P-6\ CO)^+$ ion gave the formula as $C_{26}H_{20}N_2Fe_2$, which was consistent with the chemical analysis. Mass measurement of the two most abundant ions m/e 266 and m/e 133 yielded the formulae $(C_6H_5)_2Fe_2$ and C_6H_5Fe respectively. The former ion was formed by two successive eliminations of benzonitrile from the $(P-6CO)^+$ ion, m/e 472, and supported by metastable transitions at m/e 288.4* and 191.7*. In addition the ion m/e 210, which corresponded to $(C_6H_5)_2Fe$, had two modes of formation, one by elimination of benzonitrile followed by an iron atom from m/e 369, the other showed elimination of iron followed by benzonitrile. One further fragmentation process occurred from m/e 266, accounting for the formation of m/e 188 by loss of benzene and m/e 132 by a further loss of iron.

It had been noticed in the spectrum of benzophenone-azine itself, that an ion of low abundance occurred at m/e 257, formed by elimination of benzonitrile from the parent ion and accompanied by a phenyl migration. Studies of the mass spectra of certain alkyl and aryl sulphonyl hydrazones (33) have also amply demonstrated this same phenyl migration and elimination of a RCN unit. Therefore

XIV a)



b)

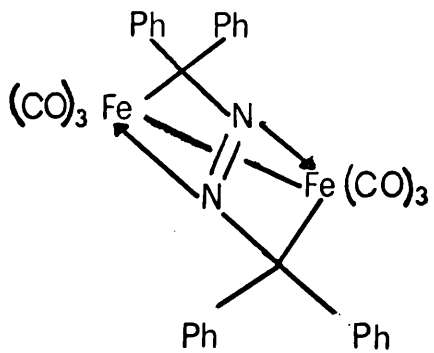
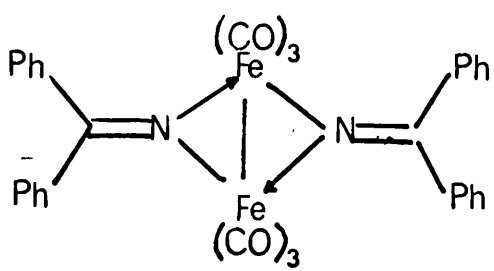


Fig 12

c)



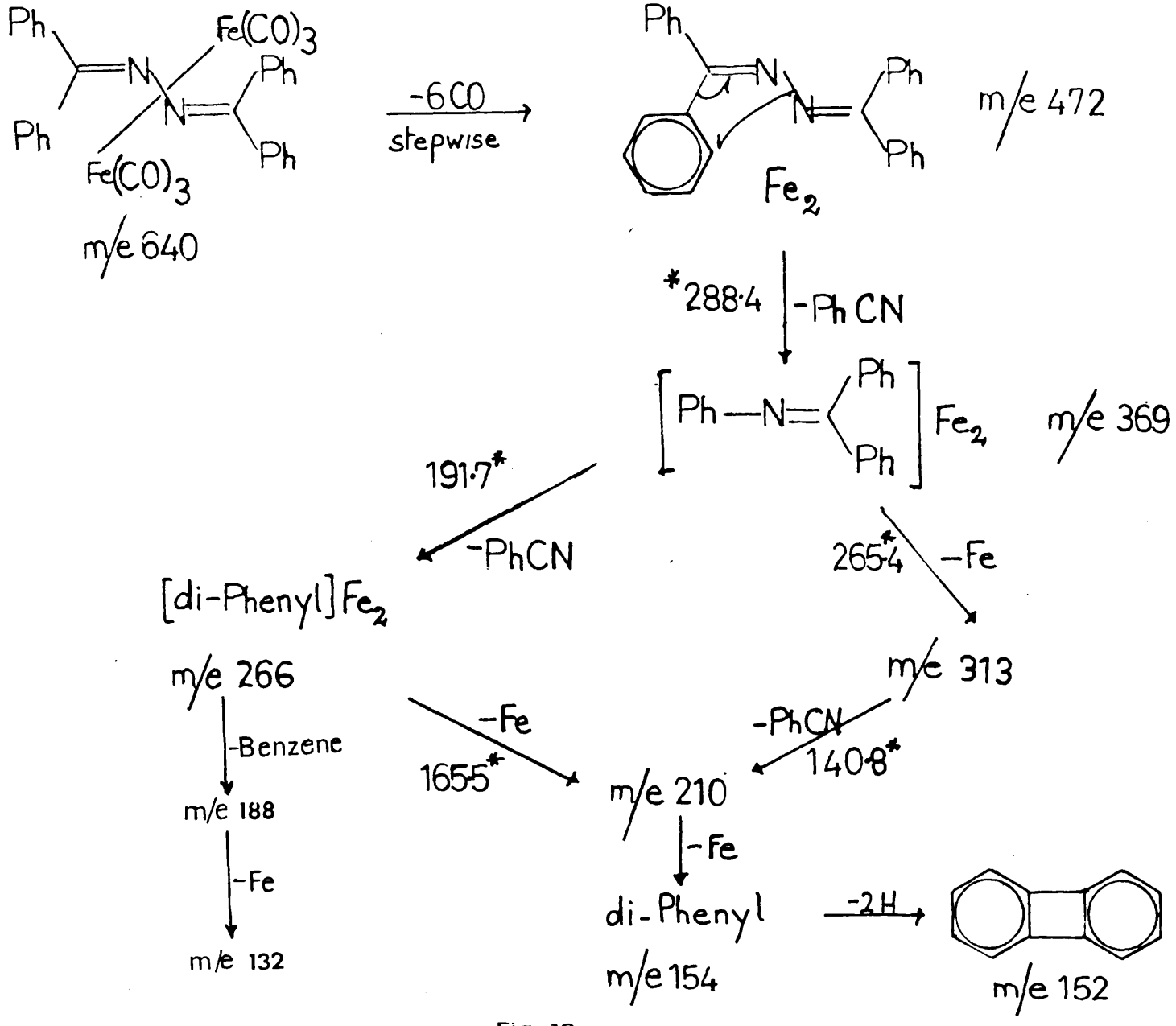

Ph
Fe(CO)3
N
Ph
Ph
N
Ph
Fe(CO)3
m/e 640
-6CO
stepwise
Ph
N
Ph
N
Ph
Fe2
m/e 472
*288·4
-PhCN
[Ph—N=C(Ph)(Ph)]Fe2
m/e 369
191·7*
-PhCN
265·4*
-Fe
[di-Phenyl]Fe2
m/e 266
m/e 313
-Benzene
-Fe
1655*
-PhCN
1408*
m/e 188
m/e 210
-Fe
-Fe
m/e 132
di-Phenyl
-2H
m/e 154
m/e 152

Fig. 13

on the basis of this information two structures were proposed XIV (a) and (b) (Fig. 12) which seemed to satisfy most of the evidence available; the proposed fragmentation pattern is shown in Fig. 13.

Further X-ray crystallographic work on this compound (34), has very recently shown that this original structure contained one fundamental error:- that of a nitrogen - nitrogen bond. The structure is in fact as shown in Fig. 12 (XIV (c)), containing two benzophenoniminato groups bridging two $Fe(CO)_3$ units. These ligands bridge through the nitrogen atoms and the reaction product is thus di-μ-(benzophenoniminato) bis (tricarbonyl iron). Hence it is clear that rupture of the nitrogen - nitrogen bond occurs in benzophenoneazine. Splitting of the N - N bond also occurs in the reaction of azobenzene with iron carbonyls, but whereas in the latter case rearrangement occurs to form the o - semidene skeleton, here both moieties are bonded seperately in the complex.

The molecule has idealised 2-fold symmetry. The tricarbonyl groups are eclipsed and the nitrogen

and iron atoms form a tetrahedron. The central portion of the molecule is thus similar in shape to that of $Co_2(CO)_8$. The Fe-Fe distance of 2.40Å is short when compared with carbon - bridged binuclear complexes and can be compared with the value 2.37Å found in the o - semidene complex. The average Fe - N distance is 1.94Å, which is shorter than those reported in previous structures (21), allowing the nitrogen atoms to be considered as being in the sp^2 hybridised state, whereas in the semidene and † benzalaniline structures with Fe - N distances of 1.97 - 2.00Å the hybridisation would be sp^3. In all cases the nitrogen atoms can be regarded as three electron donors.

The mechanism of electron impact induced dissociation of the complex must now be slightly modified to take account of structure. It is no longer necessary to consider the elimination of benzonitrile from m/e 472 and 369 in the light of a phenyl migration to nitrogen as has already been postulated for the complex and which must operate in benzophenoneazine itself, but rather we can consider the phenyl ring migration as involving π - bonding

†See complexes from Schiff's bases.

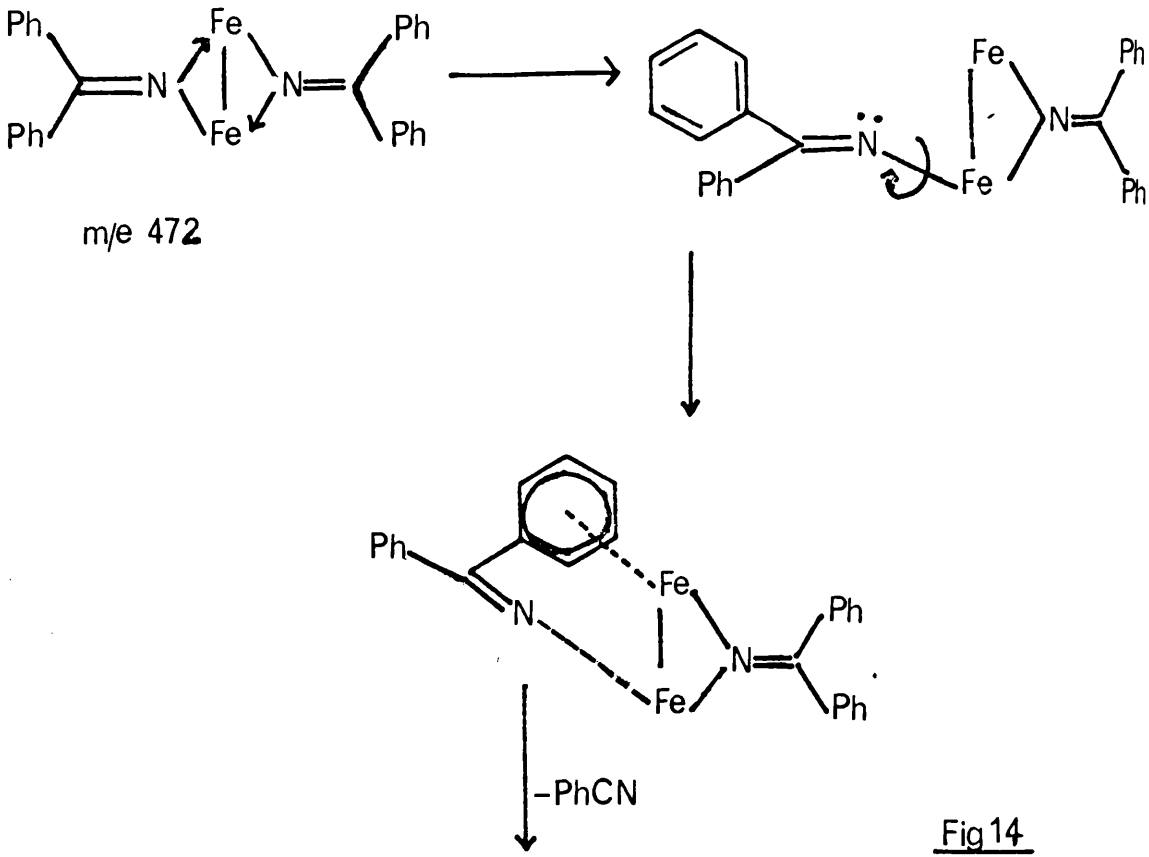

Ph
Fe
N
Ph
Ph
Fe
N
Ph
m/e 472
Fe
Ph
N
Ph
Fe
N
Ph
Ph
Fe
N
Ph
Fe
Ph
-PhCN
Fe
N
Ph
Fe
Ph
m/e 369
Fe
Fe
m/e 266

Fig 14

to one iron atom and σ-bonding to the other, as shown in Fig. 14.

The concept of metal atoms bonding by both σ and π bonds seems to be fairly common in the spectra of binuclear metal complexes (see Chapter 3) and may reflect the stability of an ion of this type relative to the uncommon neutral species of the same type.

Table 3.

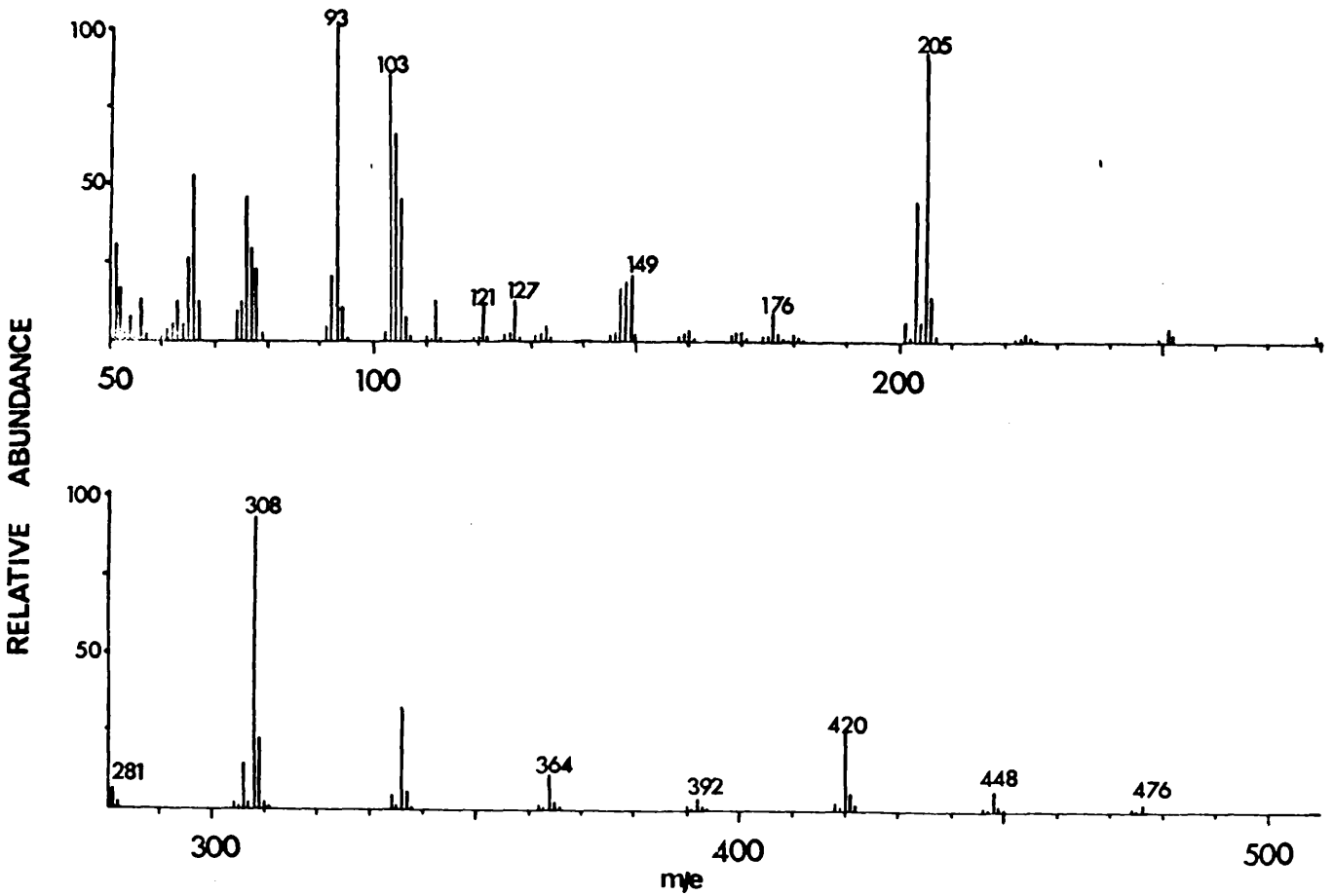
Precise mass measurements in the spectrum of the benzophenoneazine complex.

m/e	Observed Mass	Formulation	Theoretical Value	Error
472	472.03354	$C_{26}H_{20}N_2Fe_2$	472.03354	-
369	368.99036	$C_{19}H_{15}NFe_2$	368.99030	-
313	313.05557	$C_{19}H_{15}NFe$	313.05537	+0.0002
266	265.94830	$C_{12}H_{10}Fe_2$	265.94810	+0.0002
210	210.01321	$C_{12}H_{10}Fe$	210.01317	-
188	187.90112	$C_6H_4Fe_2$	187.90115	-
133	132.97412	C_6H_5Fe	132.97405	-

(c) Reactions of Aromatic phenylhydrazones with iron carbonyls

In view of the fact that nitrogen - nitrogen cleavage had been shown to occur in both azobenzene and and benzophenoneazine during their reaction with iron

Complex from B. Phenylhydrazone



carbonyls, it was decided to determine whether or not such behaviour could arise in other systems under similar reaction conditions. For this purpose aromatic phenylhydrazones were chosen, as structurally they are intermediate between azobenzenes and benzophenoneazines.

Reaction of benzaldehyde phenylhydrazone with iron enneacarbonyl produced an orange red complex which gave a molecular ion at m/e 476 (line diagram opposite). Mass measurement established its formula as $C_{19}H_{12}N_2O_6Fe_2$ and as it eliminated six carbonyl groups in consecutive decomposition to form m/e 308, the complex was judged to have the stoichiometry of (benzaldehyde phenylhydrazone) $Fe_2(CO)_6$. A benzaldehyde phenylhydrazone ligand system, however, was thought unlikely after consideration of the decomposition processes of the $(P-6CO)^+$ ion. This particular ion showed fragmentation by three possible routes:

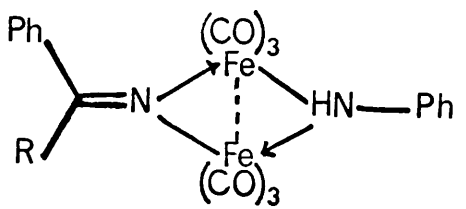
(a) Elimination of hydrogen cyanide to form m/e 281.

(b) Elimination of benzonitrile to form m/e 205.

(c) Elimination of FeH to form m/e 251.

Process (a) was followed by either loss of iron giving m/e 225 which in turn showed fragmentation by loss of C_6H_5NH to give m/e 133 (C_6H_5Fe); or by elimination of

XV



(a) R = H

(b) R = Me

Fig 15

C_6H_6 to form m/e 203 ($C_6H_5NFe_2$). All formulations were confirmed by precise mass measurement. M/e 203 was formed in addition in process (b) by elimination of 2 hydrogens from m/e 205.

It will be recollected that the complex XIV (c) demonstrated either two consecutive losses of benzonitrile from the $(P-6CO)^+$ followed by elimination of iron; or elimination in the order benzonitrile, iron, and benzonitrile to give the same fragment ion m/e 210 $(C_6H_5)_2Fe$ for which a double $\sigma - \pi$ bonded system was proposed.

On this basis, therefore, it was difficult to rationalize the mass spectral cracking of the $(P-6CO)^+$ in the benzaldehyde phenyl hydrazine complex unless a related structure XV (a) was postulated in which the two moieties formed by dissociation of the nitrogen - nitrogen bond are bonded separately to the iron atoms.

Process (a) can then be visualised as forming a $\sigma - \pi$ bonding system to iron, as in the fragment ion m/e 369 of XIV(c), followed by elimination of iron and the other ligand PhNH. Similarly process (b) forms a hydrogen bridge structure to iron followed by rearrangement and the elimination of two hydrogens to form m/e 203.

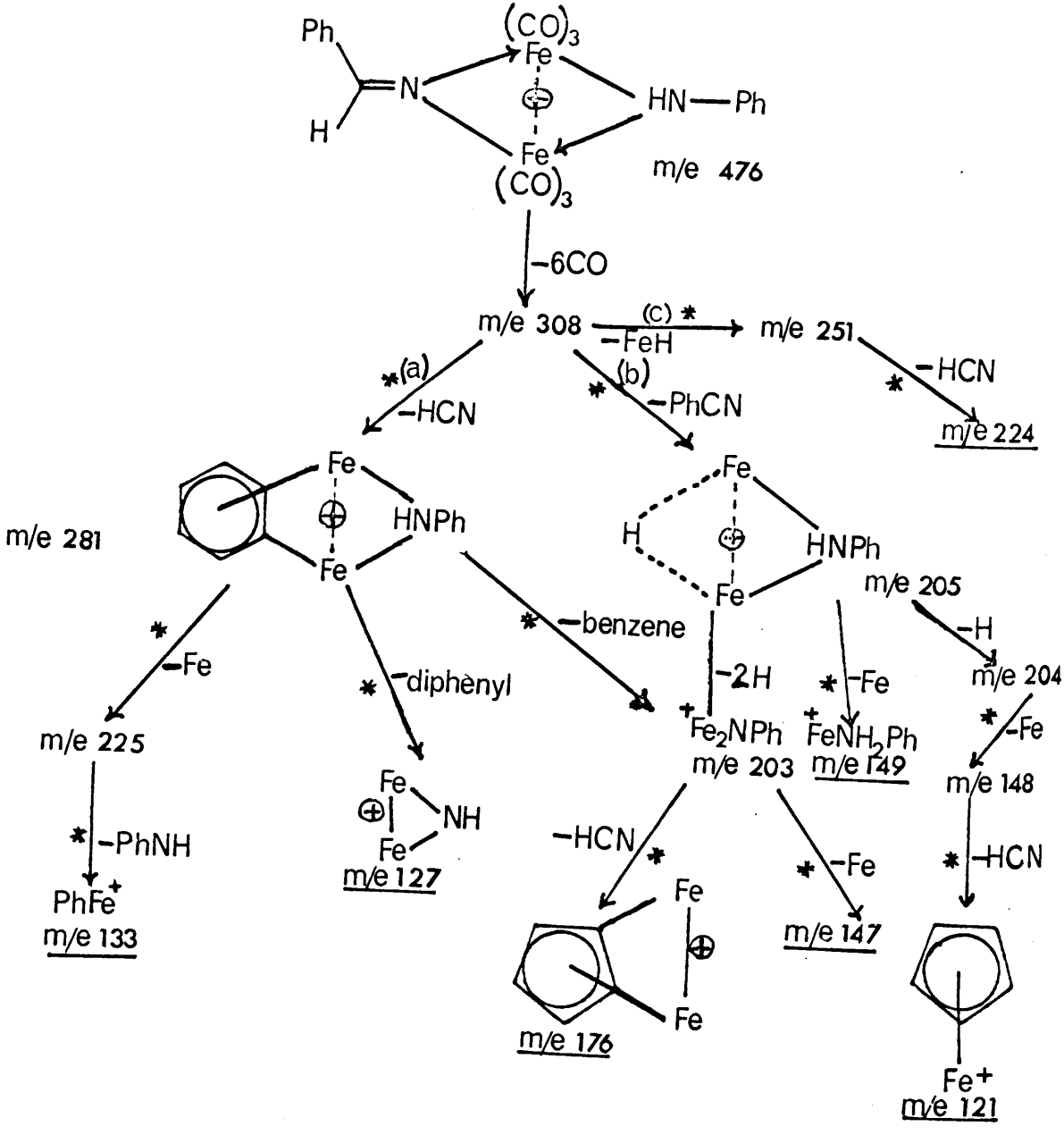

Ph
(CO)3
Fe
N
H
HN—Ph
Fe
(CO)3
m/e 476
-6CO
m/e 308
(c) *
-FeH
m/e 251
-HCN
m/e 224
*(a)
-HCN
*(b)
-PhCN
m/e 281
Fe
HNPh
Fe
H
Fe
HNPh
Fe
m/e 205
-H
m/e 204
-Fe
m/e 148
-HCN
-Fe
m/e 225
-PhNH
PhFe+
m/e 133
-diphenyl
Fe
NH
Fe
m/e 127
-benzene
-2H
Fe2NPh
m/e 203
-Fe
FeNH2Ph
m/e 149
-HCN
-Fe
m/e 147
Fe
Fe
m/e 176
Fe+
m/e 121

Fig 16

The full cracking pattern for this complex on the basis of structure XV (a) is shown in Fig. 16. In addition to the rearrangement processes already discussed, several other interesting features of the mass spectrum are worthwhile mentioning. The ion m/e 127 (Fe_2NH), for example, is formed by a process supported by an appropriate metastable ion which involves elimination of $(C_6H_5)_2$ from m/e 281. The reverse process i.e. formation of $(C_6H_5)_2^+$ is common in aromatic systems like benzalaniline, azobenzene, etc. (17), but in m/e 127 the positive charge remains within the metal system.

In addition m/e 281 demonstrates the elimination of C_6H_6 to form m/e 203, which necessarily involves hydrogen transfer from the opposite ligand system. This is to be compared with the elimination of benzene from the $(P-6CO)^+$ and $(P-6CO - Fe)^+$ ions of the complex from benzalaniline and iron enneacarbonyl discussed later in this chapter.

In a further study, acetophenone phenylhydrazone was reacted with iron enneacarbonyl and a complex of similar structure XV (b) was isolated. In general the same characteristic cracking pattern of

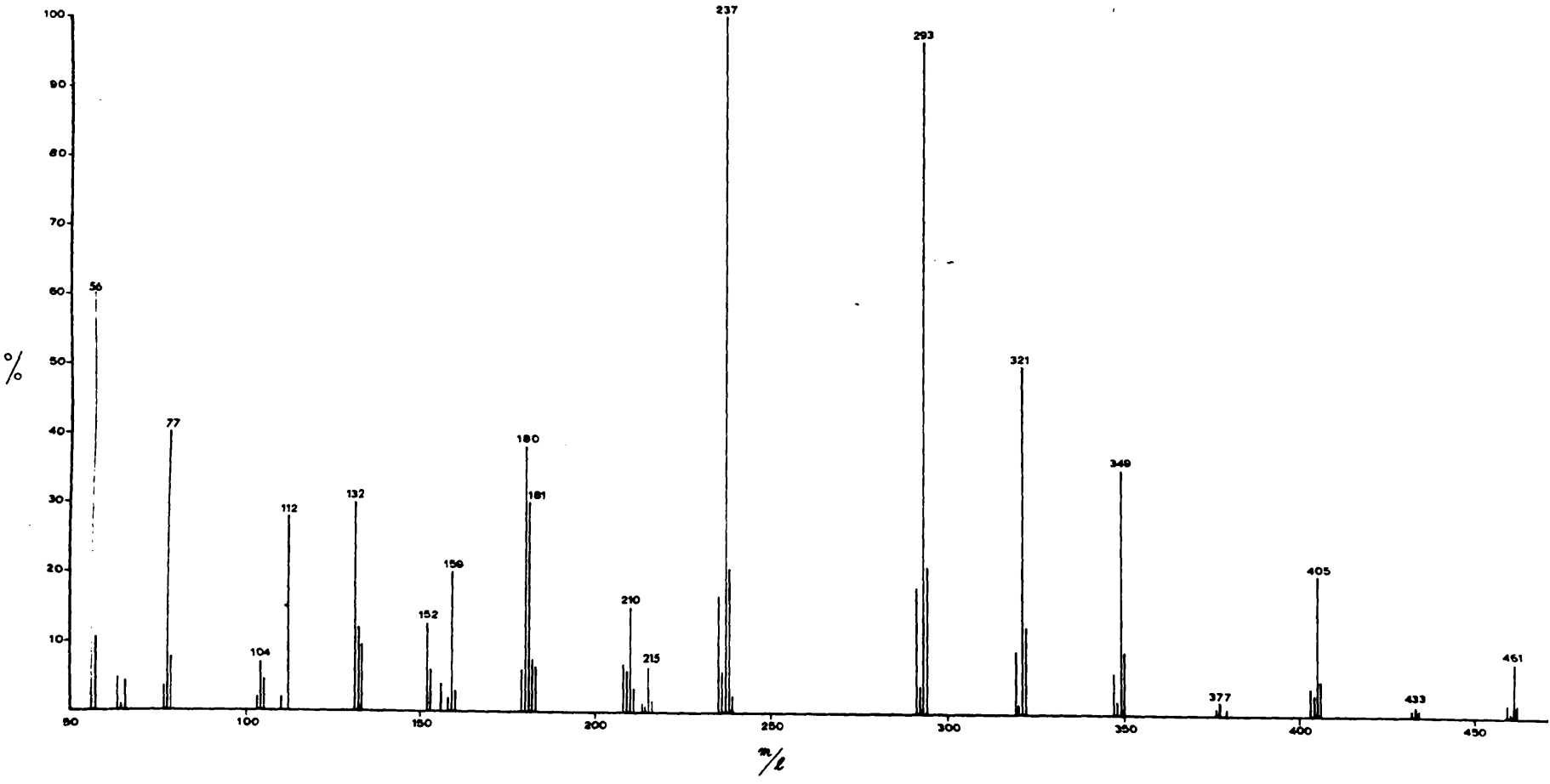
XV (a) was observed except that process (b) was very minor in comparison to process (a). This is no doubt due to the low ability of methyl groups to act as bridges in metal - metal systems. Hydrogen, however, is well known to bridge in electron deficient compounds such as boranes, and also in first row transition metal systems (35), and additional evidence has been found for the existence of hydrogen bridges in the fragment ions of binuclear metal complexes (see Chapter 3).

That the structures proposed for complexes XV (a) and XV (b) are correct has been verified by X-ray crystallography (36), and thus provides more evidence for the ability of iron carbonyls to cleave nitrogen - nitrogen bonds. The mechanism of these reactions are not only of considerable academic interest, but it may be possible to use such organometallic complexes as intermediates in synthetic schemes. Tables of mass measurements performed on the complexes are given in Table 4.

TABLE 4

m/e	Observed Mass	Formula	Theoretical Value
476	475.93926	$C_{19}H_{12}N_2O_6Fe_2$	475.93938
308	307.96972	$C_{13}H_{12}N_2Fe_2$	307.96990
281	280.95890	$C_{12}H_{11}NFe_2$	280.95890
251	251.02622	$C_{13}H_{11}N_2Fe$	251.02714
225	225.02475	$C_{12}H_{11}NFe$	225.02407
205	204.92685	$C_6H_7NFe_2$	204.92770
176	175.90112	$C_5H_4Fe_2$	175.90115
147	146.97652	C_6H_5NFe	146.97712
133	132.97403	C_6H_5Fe	132.97405
127	126.88104	$NHFe_2$	126.88075
121	120.97405	C_5H_5Fe	120.97405

COMPLEX FROM BENZALANILINE

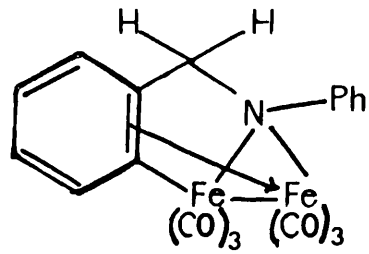


(d) Reactions of Schiff Bases with Iron Carbonyls.

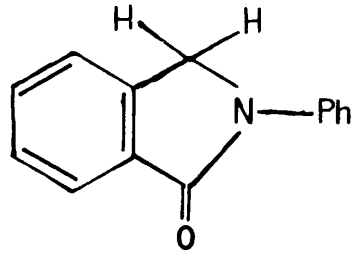
In addition to investigations in di-nitrogen ligand systems it was decided to react N-benzylidene aniline with di-iron enneacarbonyl in benzene to determine whether or not any bonding could occur in mono nitrogen systems.

A complex was indeed isolated which had no relationship whatsoever to the previous cases. The compound gave a molecular ion at m/e 461 corresponding to a molecular formula of $C_{19}H_{11}Fe_2NO_6$. Six successive stepwise losses of carbon monoxide supported by the appropriate metastable transitions established the complex as of the type, (ligand) Fe $(CO)_6$. The N.M.R., however, had already suggested that there was an objection to a structure of the type (benzalaniline) $Fe_2(CO)_6$ as there were only nine aromatic protons (τ = 2.45) and two methylene protons (τ = 5.59).

Benzalaniline itself shows a $(P - HCN)^+$ ion in the mass spectrum (17), as did the $(P - 6CO)^+$ ion of the complex. The complex, however, eliminated benzene from $(P - 6CO)^+$ which required hydrogen migration to phenyl supported the idea that methylene protons were present. The structure proposed was as shown (XVI Fig. 17), and in order that both irons attain the electronic configuration



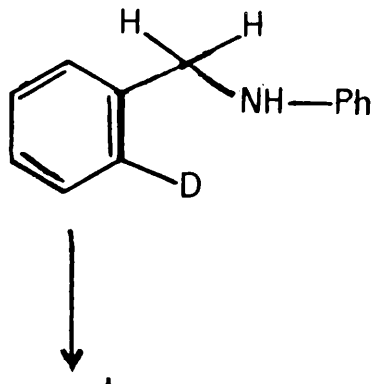
XVI

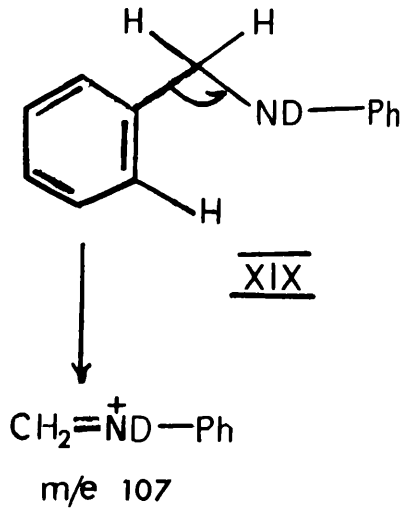


XVII

Fig. 17

XVIII





XIX

Fig. 18

of the next inert gas, one must visualize the donation of one pair of electrons from the aromatic ring to one iron. Although the complex appeared to be diamagnetic (n.m.r) a structure without π - donation from the aromatic ring to one iron would require this iron atom have only sixteen outer electrons.

Further degradative chemical work was performed on this complex. Reaction with $FeCl_3$ produced a white, crystalline compound which gave a molecular ion at m/e 209 and which mass measurement showed to be $C_{14}H_{11}NO$. It was deduced from the mass spectrum that this compound had the structure XVII, the parent molecular ion demonstrating loss of carbon monoxide followed by hydrogen cyanide to give the very stable ion m/e 152 (II) already mentioned. Comparison with a synthetically prepared sample of XVII established its identity, and suggested that iron had been bonded between nitrogen and one benzene ring. In addition lithium aluminium deuteride reduction of the complex gave a mixture of XVIII and XIX containing 81% deuterium. That the iron had been bonded to one benzene ring was demonstrated by the incorporation of one deuterium on the benzene ring in XVIII. Further synthetic work

established certain requirements for complex formation. Only those Schiff's bases derived from an aromatic aldehyde or ketone would react with di-iron enneacarbonyl. Thus acetone anil and acetaldehyde anil failed to give complexes, but acetophenone anil reacted in the expected manner. The nature of the amine used for Schiff base formation with the aromatic aldehyde or ketone also appeared to be unimportant, and N benzylidene methylamine gave a complex, albeit in low yield. It was further observed that the aromatic aldehyde or ketone should contain at least one proton ortho to the carbonyl function. Therefore, although the Schiff's base from o - chlorobenzaldehyde reacted with di-iron enneacarbonyl; that from 2, 6 - dichlorobenzaldehyde would not react.

It should be noted, however, that this assumption may not now be valid. Very recent work on the mechanism of formation of the complex has indicated that pentafluoro N-benzylidene aniline forms a complex of the same basic structure as the other anils. This reaction proceeds with the elimination of a fluorine atom and hydrogen attachment to the carbon bridge. The origin of the hydrogen was assumed to be the solvent and so the reaction with N-benzylidene aniline was repeated in hexadeuterobenzene as

solvent. The mass spectrum of this compound, however, showed no incorporation of deuterium on the methylene bridge. Similarly the complex prepared from N - benzylidene pentadeutero aniline in hexadeuterobenzene showed no incorporation of deuterium. This evidence was in conflict with that obtained from N - pentafluoro benzylidene aniline and it was decided that either two separate mechanisms were in operation or that some kind of disproportionation reaction was taking place.

In an attempt to clarify the problem, the anil of α deuterobenzaldehyde (37) was synthesised containing 66% deuterium. Reaction then with iron enneacarbonyl in benzene produced a complex which contained the same isotopic purity of monodeuterated complex, indicating that no disproportionation reaction had taken place and that the mechanism of the reaction had taken place by hydride transfer from the o position of the anil. Further supporting evidence was obtained when the anil prepared from α deuterobenzaldehyde and D_7-aniline containing 100% on the N - phenyl ring and a composition of 6:3 deuterium to hydrogen on the carbon bridge was reacted with iron enneacarbonyl in hexadeuterobenzene. The complex obtained showed only incorporation of hydrogen from the o - position

of the ring and no incorporation of deuterium from the solvent.

As no other site of hydrogen was present it was concluded that this was the correct mechanism.

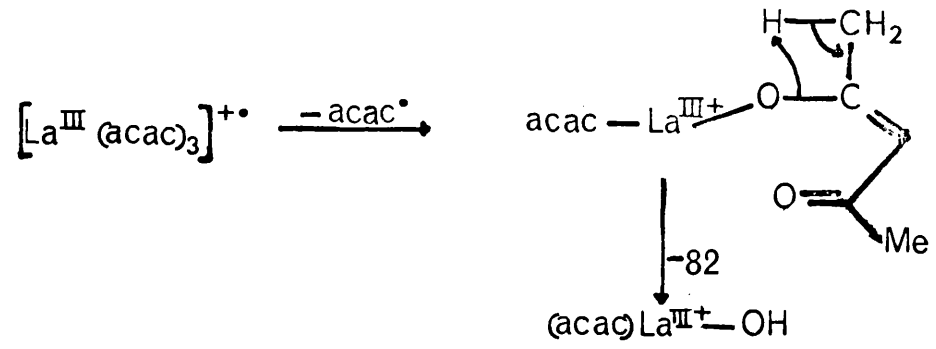
These facts provided additional strong chemical evidence for bonding between the benzene ring and an iron atom, and convincing physical evidence for the bonding in this type of complex was obtained from the Mossbauer spectra, which indicated a difference in the electronic environment of each iron atom, and hence excluded any symmetrical structure. Finally X-ray crystallographic determinations (21) have shown the structure to be correct. Although the carbons of the phenyl ring which form part of the ring are equidistant from one iron (2.3Å), the methylene group which cannot participate in bonding with the metal is bent away (2.6Å), whilst the nitrogen moves towards the iron so that it lies equidistant from both iron atoms (1.96Å). If we assume that the nitrogen acts as a 3 electron donor, then simple valence bond structures can be written which account for the symmetrical bridging by nitrogen.

Discussion of Mass Spectral Features of Related Anil Complexes

As has already been mentioned, the complex formed from N - benzylidene aniline and di-iron enneacarbonyl eliminates a benzene molecule from the $(P - 6CO)^+$ ion. Normally the most important primary process resulting from electron impact on aliphatic amines involves simple cleavage of the carbon - carbon bond adjacent to the nitrogen atom (38) and it was upon this basis that the degradation product obtained by thelithium aluminium deuteride reduction of the complex was deduced to be a mixture of XVIII and XIX as shown in Fig. 18.

The ion formed by primary β fragmentation of amines normally undergoes further fragmentation and hydrogen rearrangement with elimination of a neutral molecule, (38). The site of hydrogen transfer was formerly considered to be the β carbon involving a four membered transition state but Djerassi et al(39) have shown that four, five and six membered transition states are possible in the hydrogen migration and that the hydrogen transferred is non specific.

Some emphasis has been placed on the fact that this non specific migration of hydrogen is a secondary


[La^III (acac)3]+•
−acac•
acac — La^III+
O
C
H
CH2
O
Me
−82
(acac)2 La^III+ — OH

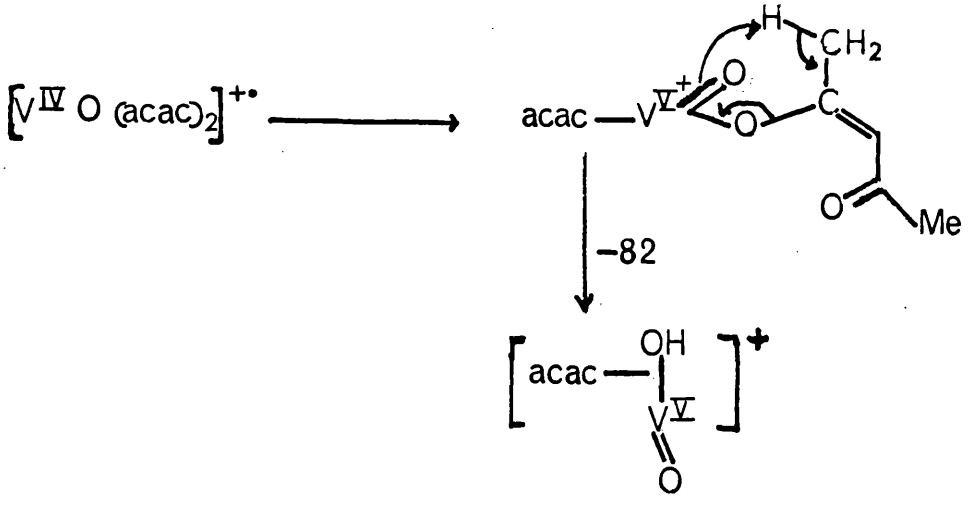

[V^IV O (acac)2]+•
acac — V^V+
O
O
H
CH2
C
O
Me
−82
[acac — OH
V^V
O]+

Fig 19

process occurring in an even electron system. In the case of the benzalaniline complex hydrogen migration with elimination of benzene is also a secondary process which occurs in both the $(P - 6CO)^+$ and $(P - 6CO - Fe)^+$ ions. If then we are to discuss the specificity or non specificity of this rearrangement process in the light of the odd or even electron nature of the complex some little difficulty arises owing to the ambiguity in consideration of the oxidation state of the metal atoms.

Recently Shannon has attempted to show (40, 41, 42) that odd electron ions can be changed to even electron systems by a change of oxidation state of the metal atom. This is claimed as, in the compounds studied, peaks due to loss of even electron fragments from a radical ion are small in comparison with those due to loss of odd - electron fragments. For example, (43) odd electrons ions of the type $\overset{n}{\text{Metal}}(acac)_n^+$ where acac = acetyl acetone typically lose the odd electron fragments $CH_3^{\cdot}$ when n = 1 or 2 or $acac^{\cdot}$ when n = 3 or 4, while even electron ions of this structure i.e. ions formed from the parent or other odd electron ions by loss of radical fragments, eliminate an even - electron fragment of mass 82 as shown for the case of $La(acac)_3$ in Fig. 19. The argument is then extended to

suggest that elimination of even electron fragments, from what one might presume to be odd electron systems, can be rationalised by first increasing the oxidation state of the metal by one, causing the metal orbital system to become an even electron variety, and hence the greater probability of eliminating an even electron fragment. The case of $VO(acac)_2$ is shown in Fig. 19. Such arguments seem very superficial indeed, in as much as it is very often an arbitary choice as to which oxidation state one considers the metal complex to be in; even in the parent ion.

Some of the difficulties can, however, be removed if classification is based upon the donor characteristics of particular ligands, assuming these to be radical species attached to a metal atom in its lowest oxidation state. For metal complexes it is usually convenient to consider the metal as zero-valent, or if the complex is charged, then the metal atom will carry the total charge.

It may be argued that it is unrealistic to consider two cyclopentadienyl radicals as each donating five electrons to a zero-valent iron atom in ferrocene,

Cyclopentadienyl Tricarbonyl Molybdenum

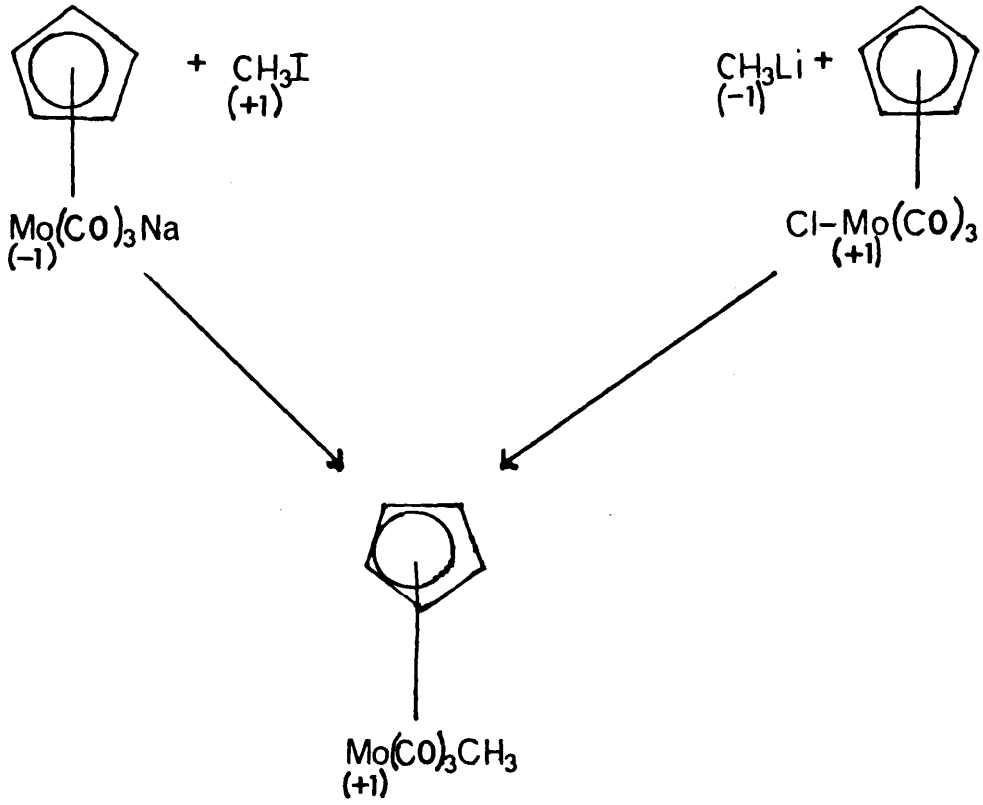


Fig. 20

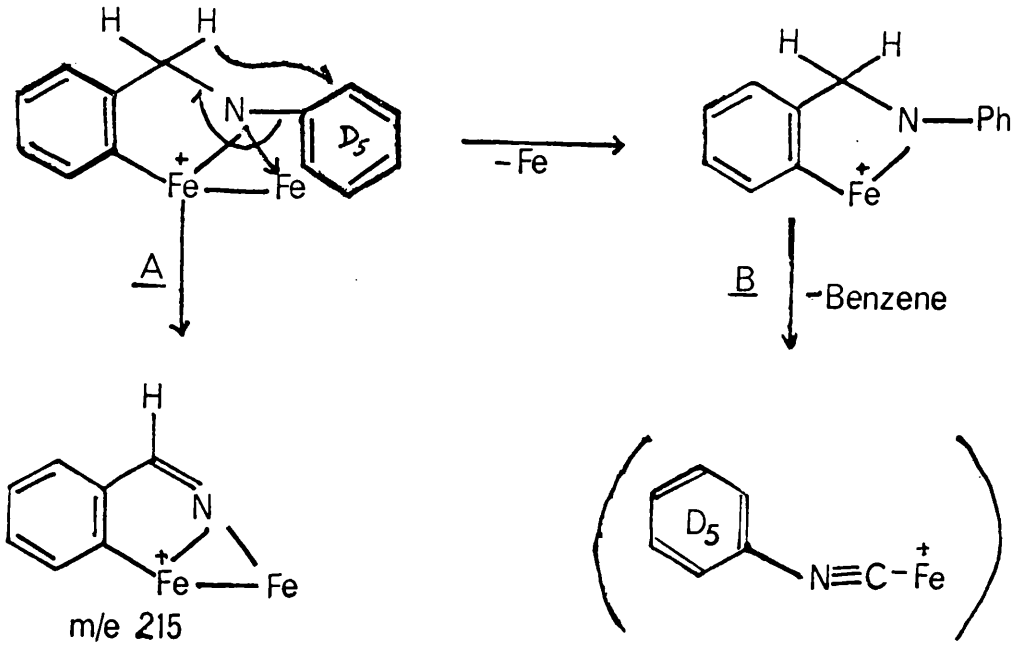
since the chemical reaction seems to suggest reaction of two cyclopentadieniel anions with ferrous iron (44). These arguments are merely tautological if one simply considers the nature of the product rather than its origin. The example of cyclopentadienyl tricarbonyl molybdenum which is shown opposite Fig. 20, clearly demonstrates the confusion which results if one does not resort to a radical system involving the metal in a zero-valent system.

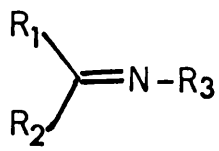
Thus one electron donors include alkyl, aryl and acyl groups and hydrogen and halogen atoms. Alkyl and aryl derivatives of Zn (45) and Pb (46) are the earliest known compounds containing one electron donor ligands. For all the derivatives of one electron donors their stabilities usually increase within a group e.g. W, Mo, Cr, and also when carbonyls are replaced by phosphines etc. A large number of groups ranging from CO, Pr_3, R_2S (R = alkyl and aryl) to amines and olefins are known to function as two electron donors. The bonding in metal carbonyl systems is discussed in the Appendix to this chapter.

If this argument is then applied to the anil complex under consideration the unionized molecule can be considered as an unsymmetrical bimetallic complex,

with the metal atoms in the zero-valent state and bonded by single electron donation from the aromatic ring, two electron donation from each carbonyl grouping, and 3 electron donation from nitrogen. The ionization potential of the molecule is of the same order of magnitute as iron itself and can be considered as the removal of an electron from one of the highest occupied molecular orbitals (T_{2g}) which are in fact those metal orbitals involved in π bonding to the antibonding orbitals of the carbonyl groups. These orbitals are almost totally metallic in character, and it is therefore useful to consider the ionization process as occurring within the metal orbital system.

On the basis of this argument the parent ion exists with one metal atom still in the zero-valent state, and the other in the +1 oxidation state. The elimination of the carbonyl groups, therefore, from the parent ion does not involve a change in the oxidation state of the metal as these are purely two electron donor bonds and we are able to view the $(P - 6CO)^+$ ion as having both iron atoms in the same oxidation states as the parent ion. Loss of iron is the major fragmentation process occurring from this ion, although benzene is eliminated to a moderate extent, i.e. both





XX

R_1 = Aryl

Fig 21

even and odd electron neutral fragments are lost.

This result of course has been obtained by an argument beginning with consideration of ionization within the molecular orbital system rather than the purely arbitrary method employed by Shannon et al.

Now it can readily be seen that it is not a cut and dried idea to consider fragmentation in the light of even or odd electron systems. Even the intensive investigations of Djerassi and his co-workers (47 - 58) into the specificity of hydrogen transfer in even or odd electron systems have disclosed certain exceptions to their proposed theories (56, 57).

Therefore, having regard to the questionable nature of mass spectrometric theory in these areas of investigation it was decided to examine the elimination of benzene with the aid of labelling techniques. For this purpose the complex was synthesised from benzaldehyde and D_7-aniline to give D_5 labelling on the N-phenyl ring.

Mass spectrometry then demonstrated that the principal transition from $(P - 6CO)^+$ with elimination of benzene involved the labelled ring according to route A, Fig. 21, with consequential N-phenyl fragmentation and hydrogen transfer from the methylene bridge. Benzene could also be eliminated to a small extent from the

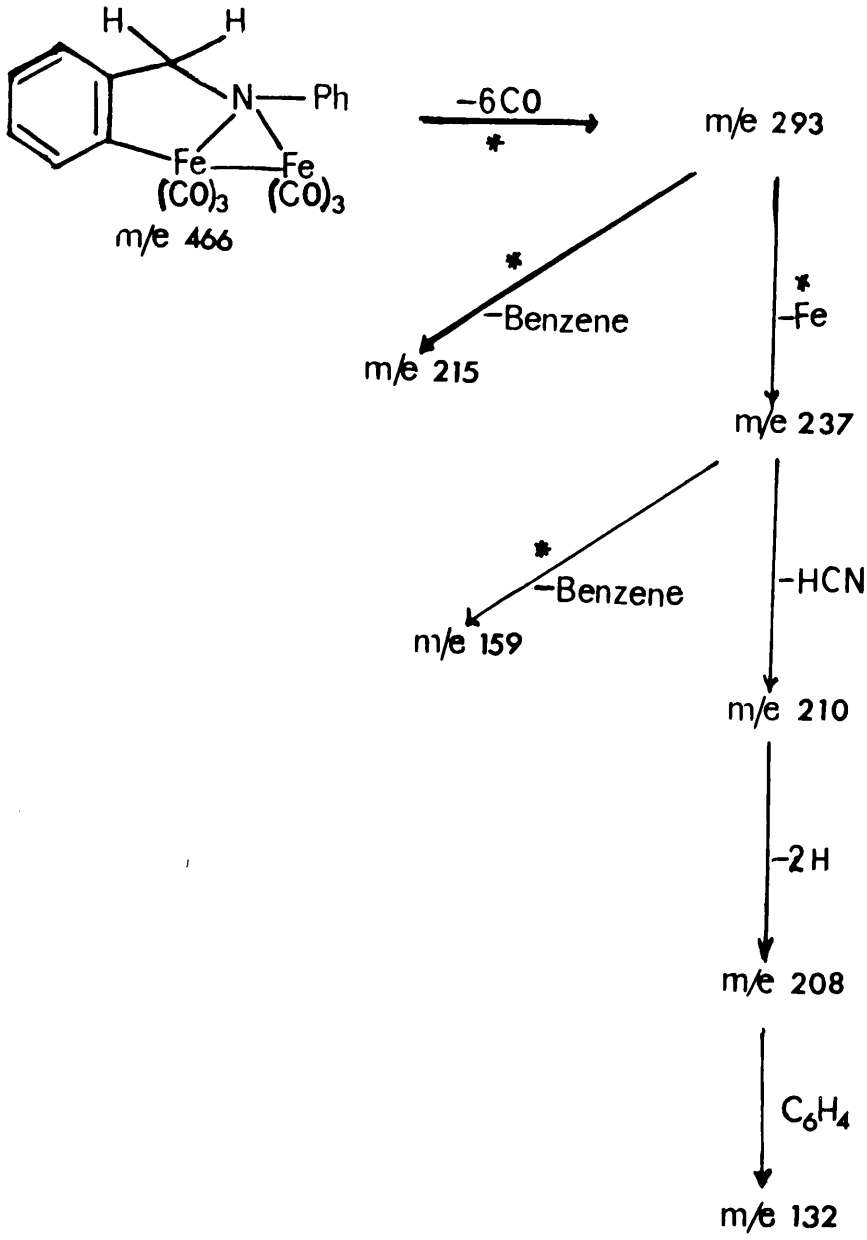
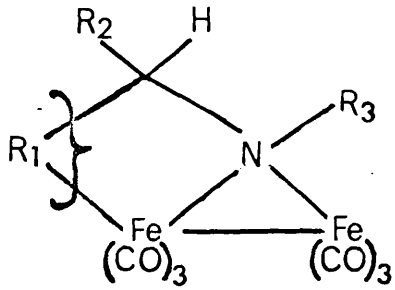

H
H
N
Ph
Fe
Fe
(CO)3
(CO)3
m/e 466
-6CO
*
m/e 293
*
-Benzene
m/e 215
*
-Fe
m/e 237
*
-Benzene
m/e 159
-HCN
m/e 210
-2H
m/e 208
C6H4
m/e 132

Fig. 22

disubstituted ring to give a weak ion at m/e 220.

The same process from $(P - 6CO - Fe)^+$, however, involved the disubstituted benzene ring entirely with the necessary transfer of two hydrogens from the methylene bridge, according to route B,(Fig. 21). It is difficult to find any reason why there should be a change in mechanism in changing from the bimetallic to mono-metallic state. It is probable, however, that the elimination of iron from $(P - 6CO)^+$ returns the nitrogen to its normal valency with a lone pair of electrons. As has already been stated, the dissociation of amines does not normally show cleavage of the nitrogen - carbon bond rather β cleavage occurs. That β cleavage does in fact occur must lend some support to the present suggestion, although no firm mechanism can be found for this elimination of benzene.

The complete mass spectrometric fragmentation pattern is shown in Fig. 22. In all the spectra of substituted complexes of this type, ions exist both for the dihydro and parent organic nuclei. Spectra run at low electron voltages show that these ions do not originate by ion impact induced dissociation of the metallic complex, but are formed thermally on the surface of the direct insertion probe.



XVI

(a) $R_1 = C_6H_4$, $R_2 = H$, $R_3 = C_6H_5$

(b) $R_1 = C_6H_4$, $R_2 = CH_3$, $R_3 = C_6H_5$

(c) $R_1 = C_6H_4$, $R_2 = C_6H_5$, $R_3 = C_6H_5$

(d) $R_1 = \underline{o}\text{-}ClC_6H_3$, $R_2 = H$, $R_3 = C_6H_5$

(e) $R_1 = \underline{p}MeC_6H_3$, $R_2 = H$, $R_3 = C_6H_5$

(f) $R_1 = C_6H_4$, $R_2 = H$, $R_3 = C_6H_4\underline{p}Me$

(g) $R_1 = C_6F_4$, $R_2 = H$, $R_3 = C_6H_5$

(h) $R_1 = C_6H_4$, $R_2 = H$, $R_3 = Me$

Effects of Substitution

Apart from the chemical evidence collected by varying the nature of the substituents R_1, R_2, R_3 on the basic skeleton of the Schiff's bases XX (Fig. 21), an opportunity was presented for studying the mass spectrometric behaviour of the derived complexes XVI(a)-(h). Various important features observed as a consequence of these structural alterations are worthy of attention.

(i) The nature of R_2.

(a) R_2 = Methyl (XVIb)

Substitution of one methylene hydrogen by methyl leaves the two main fragmentation routes unaffected, hydrogen cyanide elimination being replaced of course by that of methyl cyanide. Two additional pathways of dissociation, however, are incorporated in the mass spectrum (see Fig. 23). M/e 266, for instance, occurs directly by abstraction of methyl cyanide from the $(P - 6CO)^+$ ion. This ion occurs to an extent of 2.0%, whilst the ion from elimination of benzene is slightly more abundant (6.3%), both being even electron fragments.

The abundance of m/e 173, $(P - 6CO - Fe - benzene)^+$, is, however, much smaller than the corresponding ion in the

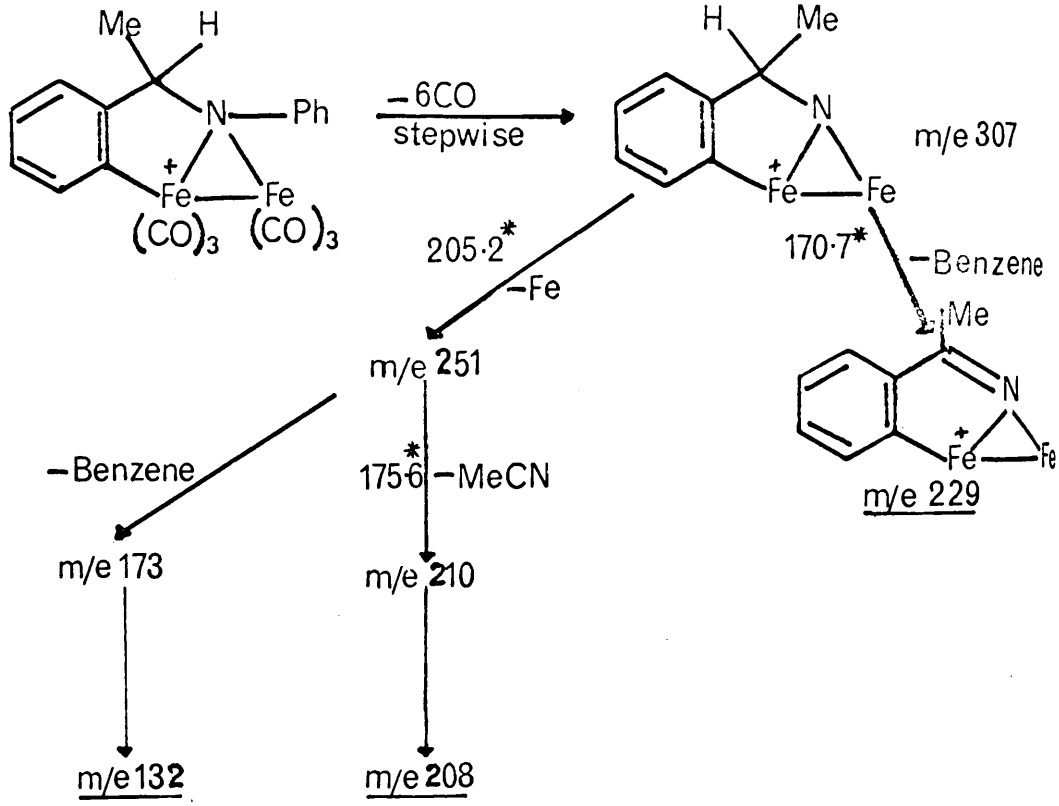
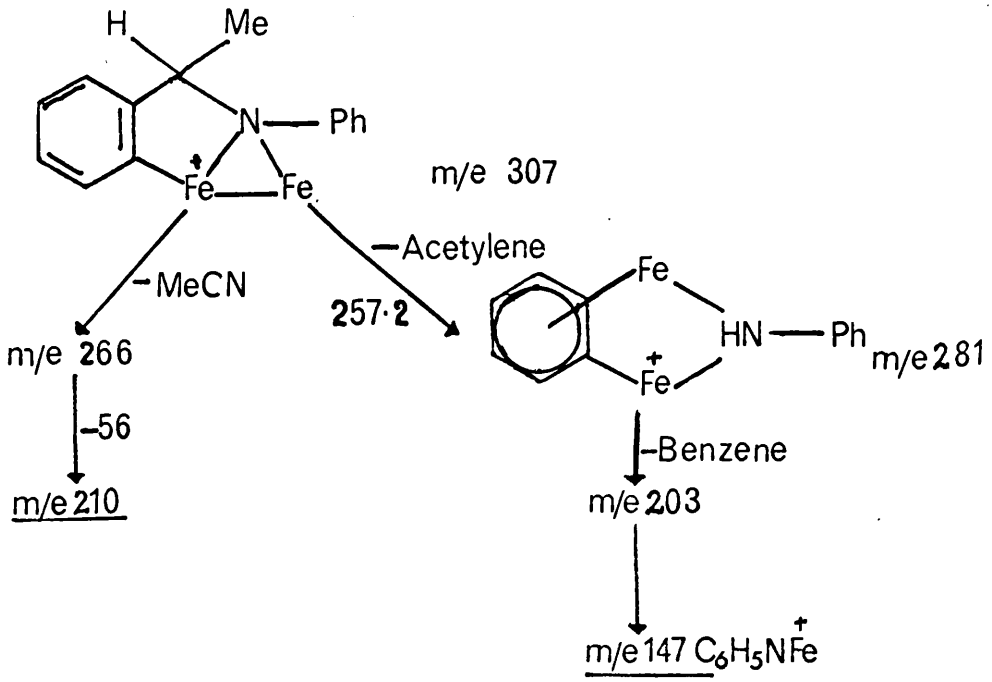


Fig 23

Additicnal routes



spectrum of the benzalandine complex, due possibly to the greater number of competing fragmentation processes which can occur from m/e 307.

The other route is more surprising. It involves the loss of twenty six mass units from the $(P - 6CO)^+$ ion and is not as was first supposed the elimination of C≡N, but of acetylene, as determined by precise mass measurement of the ions m/e 307 and m/e 281. Further mass determinations at high resolution on the ions m/e 203 and m/e 147 established their formulation as shown. This second route from m/e 281 onwards is, in fact, an integral part of the electron impact dissociation of the phenyl hydrazone complexes which has been discussed.

In order to investigate, a little more fully, the fragmentation process of acetylene abstraction it was decided to try and differentiate between a mechanism which involved the carbon - methyl bridge system and that of a possible loss from one of the benzene rings. No report has yet been made of any substituted benzenes existing in the butadienyl acetylene form (59) in the ionic state, and this possibility had obviously, to be investigated. An experiment was then devised which would not only differentiate between these two routes but at the

same time give information as to whether or not the hydrogens of the methyl group took part in any migration process during the elimination of benzene from m/e 307. This involved the synthesis of the complex from the condensation product of D_3- acetophenone (60) and N - D_2 - aniline (61).

Unfortunately difficulties were encountered in obtaining the labelled anil in good isotopic purity. The best which could be obtained on the bridging methyl by this method was an anil which mass spectrometry showed to be as follows CH_3 = 33%, CH_2D = 33%, CHD_2 = 23%, CD_3 = 12%. No change in isotopic concentration was observed in the preparation of the corresponding complex with iron enneacarbonyl.

Calculations made on the basis of these isotopic concentrations and making no allowances for isotopic effects showed that the expected ratio of the abundances of m/e 281: 282: 283 should have been 2.00: 1.20: 1 assuming that acetylene was being eliminated from the methyl bridge system with concomitant transfer of either 2H, DH or D_2 to the remaining daughter ion. In fact in the experimental measurement of these abundancies (making corrections for ^{13}C, ^{54}Fe and ^{57}Fe contributions) values of 1.99: 1.25: 1 were obtained, thus making quite clear

the nature of the rearrangement process.

Similarly in the process involving elimination of benzene from the $(P - 6CO)^+$ ions of the labelled complex, ions were observed at m/e 229 and 230 corresponding both to hydrogen and deuterium transfer. Calculations based on the assumption that all hydrogen and deuterium transferred came from the methyl group predicted that the ratio m/e 229/m/e 230 be 1.63: 1. Experimental observation showed this value to be 1.59: 1, which is very good agreement, and leaves very little doubt about the participation of the methyl group in hydrogen transfer to the phenyl ring.

(b) R_2 = Phenyl. (XVI c.)

The main effect of phenyl substitution, as might be expected, is to change the stabilities of various ions relative to the ions of the basic benzalaniline complex. For instance the base peak is now m/e 369, $(P - 6CO)^+$, as compared with benzalaniline m/e 237, $(P - 6CO - Fe)^+$. The abundancies of the ions formed by stepwise losses of carbon monoxide from the parent ion are not changed to any great extent, nor are their percentage "A" values (see Appendix to chapter 2) and we may assume that the initial ionization and dissociation processes differ very little from that of the benzalaniline complex. The stability,

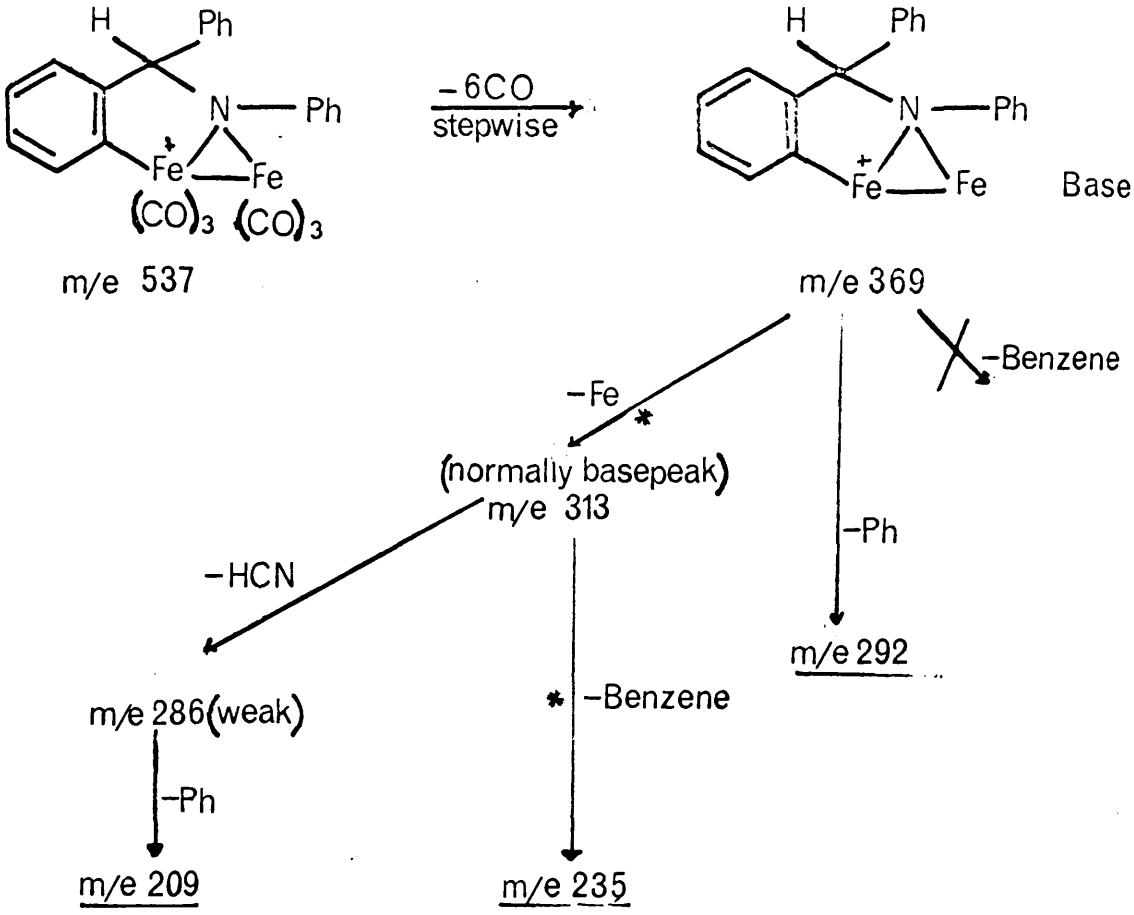

H
Ph
N
Ph
Fe
Fe
(CO)3 (CO)3
m/e 537
-6CO
stepwise
H
Ph
N
Ph
Fe
Fe
Base
m/e 369
-Benzene
-Fe
*
(normally basepeak)
m/e 313
-Ph
m/e 292
-HCN
m/e 286(weak)
-Ph
m/e 209
*
-Benzene
m/e 235

Fig 24

however, of the $(P - 6CO)^+$ ion is such that it dissociates to a very small extent. This it can do in either of two ways, one by elimination of iron, and the major process; the other by loss of phenyl as opposed to the more normal benzene (See Fig. 24). The loss of benzene in the step from the $(P - 6CO)^+$ ion, we have already shown to involve the N-phenyl ring, and obviously the presence of another phenyl group at R_2 causes a great deal of steric crowding for any attempted hydrogen migration.

The $(P - 6CO - Fe)^+$ ion, however, does show elimination of benzene, no doubt due to the change in symmetry and flexibility in the neighbourhood of the nitrogen atom. If, as we have shown for the case of the D_5 benzalaniline complex the aromatic ring involved in this decomposition is the disubstituted one, hydrogen must not only be transferred from the substituted methylene bridge but also from one, or both phenyl rings since this route requires a double hydrogen transfer.

Within the rest of the spectrum there exist ions for the $(P - 6CO - Fe - HCN)^+$ decomposition process and at m/e 210 (diphenyl iron) - an ion common to all the non aromatic substituted complexes, though these are small

in comparison with the ions due to thermal degradation and electron impact dissociation of benzophenone anil (parent ion at m/e 255) on the surface of the direct insertion probe.

(ii) The Nature of R_1.

(a) R_1 = o - chloro phenylene (XVI d)

The mass spectrum of most aromatic chlorine compounds normally displays a $(P - Cl)^+$ ion as base peak for substituents bigger than methyl (62). The mass spectrum of the complex derived from o - chlorobenzalaniline admirably demonstrates the fallacy in extending known fragmentation routes of organic compounds to the organometallic systems derived from them. Organometallic compounds, as has already been discussed in some detail, cannot merely be considered as organic nuclei attached by weak bonds to metallic units, dissociation under electron impact of which should show elimination of the weakly bonded metal, followed by normal fragmentation of the organic ligand. Metal atoms have obviously a great effect, not only on the reactivity and chemical nature of the complex, but also on their physico - chemical properties.

Similarly, substitution within the organic ligand also effects these properties. In the complex under consideration, the basic "benzalaniline complex

o-Chlorobenzalaniline Complex

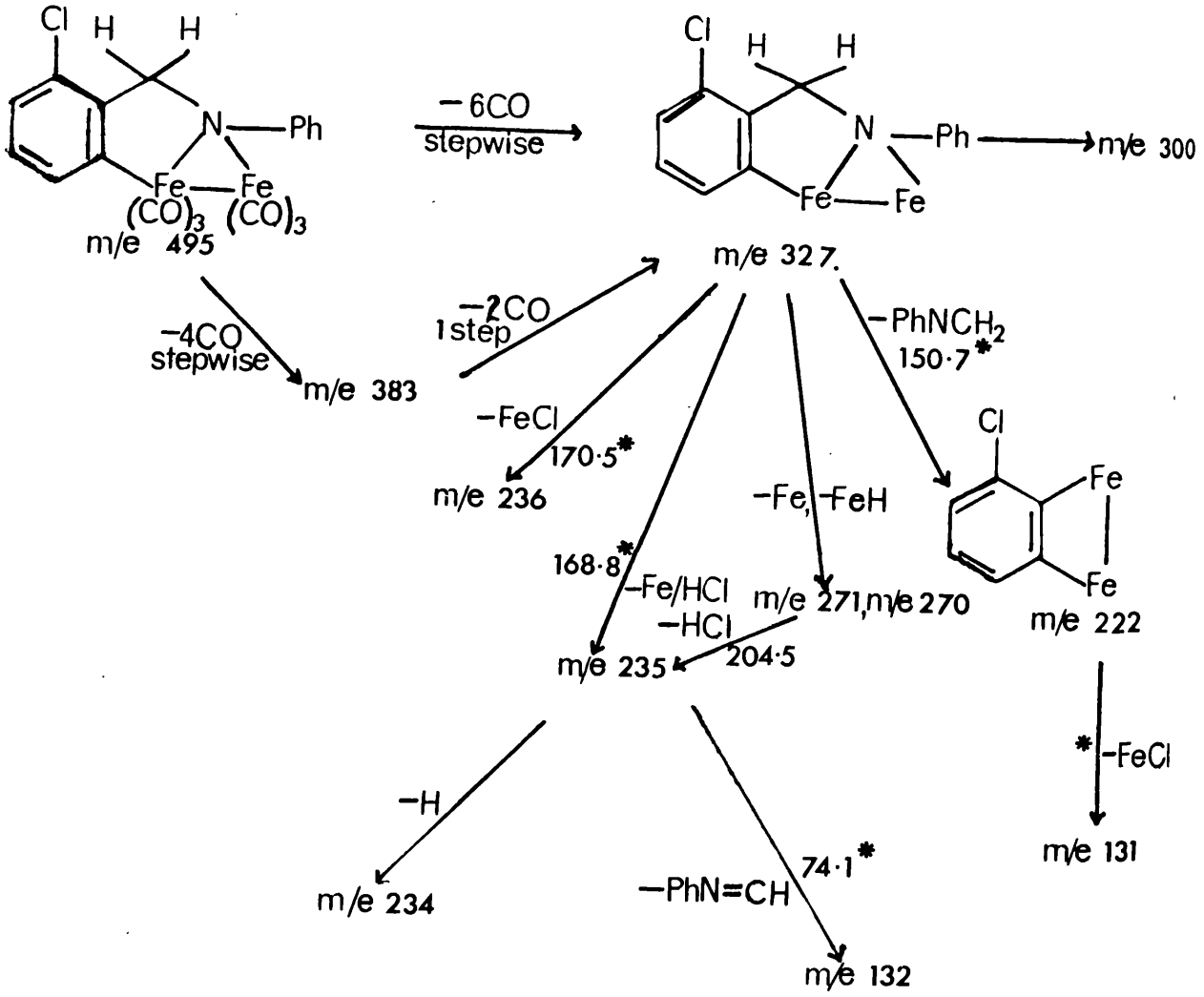
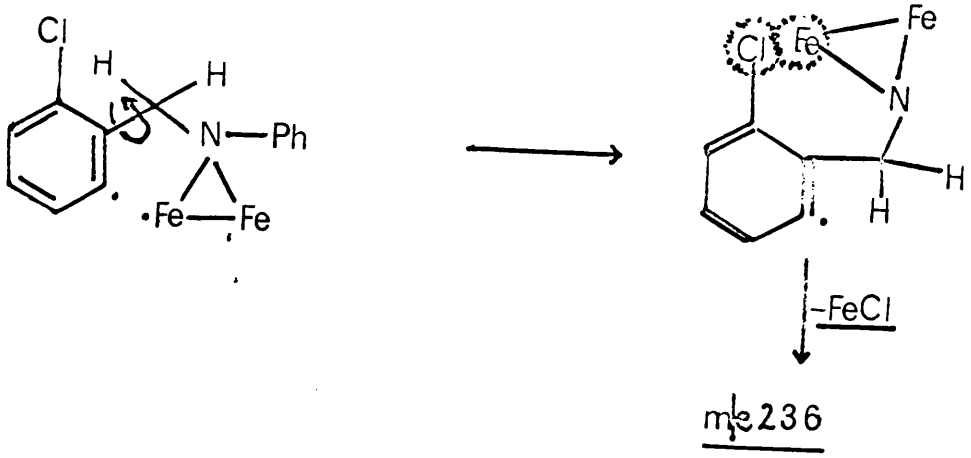


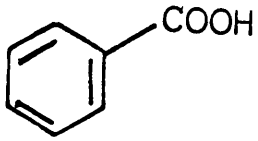
Fig. 25

type" breakdown almost completely disappears; that is to say no elimination of benzene occurs at all and instead a process involving loss of $PhCH_2N$ is observed from the $(P-6CO)^+$ ion at m/e 327. Even the systematic stepwise fragmentation of carbonyl groups from the parent ion is changed since there is evidence (m^*= 334.1 and m^*= 279.2) for simultaneous elimination of two carbonyl groups between m/e 439 and m/e 383 and between m/e 383 and m/e 327. That these effects are not evident in any other complexes of a similar type must be due to the influence of o - chlorosubstitution (see Fig. 25).

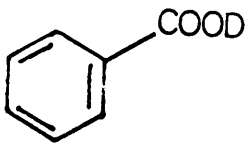
It is a commonly observed feature that the stability of the neutral fragment eliminated, together with the stability of the fragment ion formed, are important considerations in the feasibility of a decomposition process taking place. Hence m/e 222, which is an abundant ion(22%)showing no further decomposition must be exceptionally stable relative to the neutral fragment $PhCH_2N$ eliminated during its formation from m/e 327. This neutral fragment, however, need not be a single radical and if it can be considered as the concomitant elimination of benzene and hydrogen cyanide then the thermodynamic balance of the decomposition becomes doubly favourable. Such simultaneous eliminations are not without



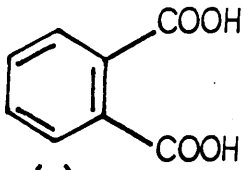
A.



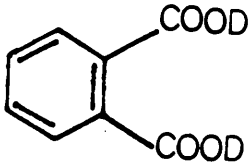
(1)



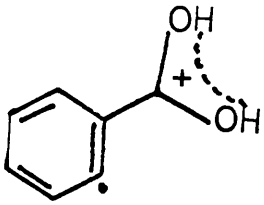
(2)



(3)



(4)



(5)

Fig 26

precedent (63, 64) though they comparatively seldom occur, which makes the dissociation of the complex all the more unusual.

Metastable ions at m/e 168.8 and 170.3 represent elimination of Fe/HCl and Fe/Cl from m/e 327. The latter is, however, probably the elimination of FeCl as a complete unit. This is possible if we assume homolysis of the bond between iron and chloro-substituted ring, followed by rotation about the bond as shown in Fig. 26. An accurate three dimensional model of the compound using X-ray data from the corresponding benzalaniline complex (21) and a carbon - chlorine bond length of 1.73Å shows iron-chlorine overlap to be unavoidable if such rotation occurs. Beynon (65) who has studied the mass spectra of various mono and o - dibasic aromatic acids (Fig. 26A) has shown that deutero benzoic acid demonstrates OH and OD losses and (5) is postulated as an intermediate rotation of the C - C bond producing an equilibrium exchange of hydrogen between the o - position and the carbonyl. The molecule ion of 4 however only eliminates OD since sterically the rotation is restricted by the o - carboxylic acid group. However, after a loss of carbon dioxide the molecule is no

longer sterically hindered and there is the possibility of both OH and OD loss such as occurs in benzoic acid.

That such rotational intermediates do exist is fair evidence in support of the elimination of FeCl as an entity. Further support is to be found in the spectrum at m/e 91 which precise mass measurement has shown to be $(FeCl)^+$.

The fragmentation step which involves the formation of m/e 235 by concomitant elimination of iron and hydrogen chloride can be visualised as forming a substituted benzyne ion which further dissociates by elimination of 103 mass units to give the ion m/e 132, common to all the spectra of the Schiff's base complexes. This latter process is supported by a metastable transition at m/e 74.1.

It should also be noted here that although o - chloro benzalaniline is liberated on pyrolysis within the mass spectrometer and that the electron impact induced dissociation of this compound produces the ions m/e 180 and m/e 152 (II) as expected, the complex shows no elimination of chlorine as such, either in the parent or its fragment ions, nor are there present any ions related to m/e 210, $(C_6H_5)_2Fe$, in the spectrum of the benzalaniline

complex. A table of mass measurements performed on this complex is shown below.

TABLE 5

m/e	Observed Mass	Formula	Theoretical Value
271	270.98482	$C_{13}H_{10}NClFe$	270.98510
236	236.01618	$C_{13}H_{10}NFe$	236.01625
222	221.86110	$C_6H_3ClFe_2$	221.86118
132	131;96683	C_6H_4Fe	131.96622
131	130.95892	C_6H_3Fe	130.95840
91	90.90432	FeCl	90.90378

(b) The Complexes from N - 4 Benzylidene Aniline(XVIe) and N benzylidene p - Toluidine (XVI f)

Although the complex from N benzylidene p - Toluidine is essentially a variation in the substituent R_3, it is worthwhile to discuss its mass spectral features together with its isomeric complex XVIe as the spectra of the two compounds are almost identical.

Both show the main features already observed for the complex from benzalaniline; that is stepwise loss of all six carbonyl groups forming the ion m/e 307,

N-4 Methyl Benzylidene Aniline

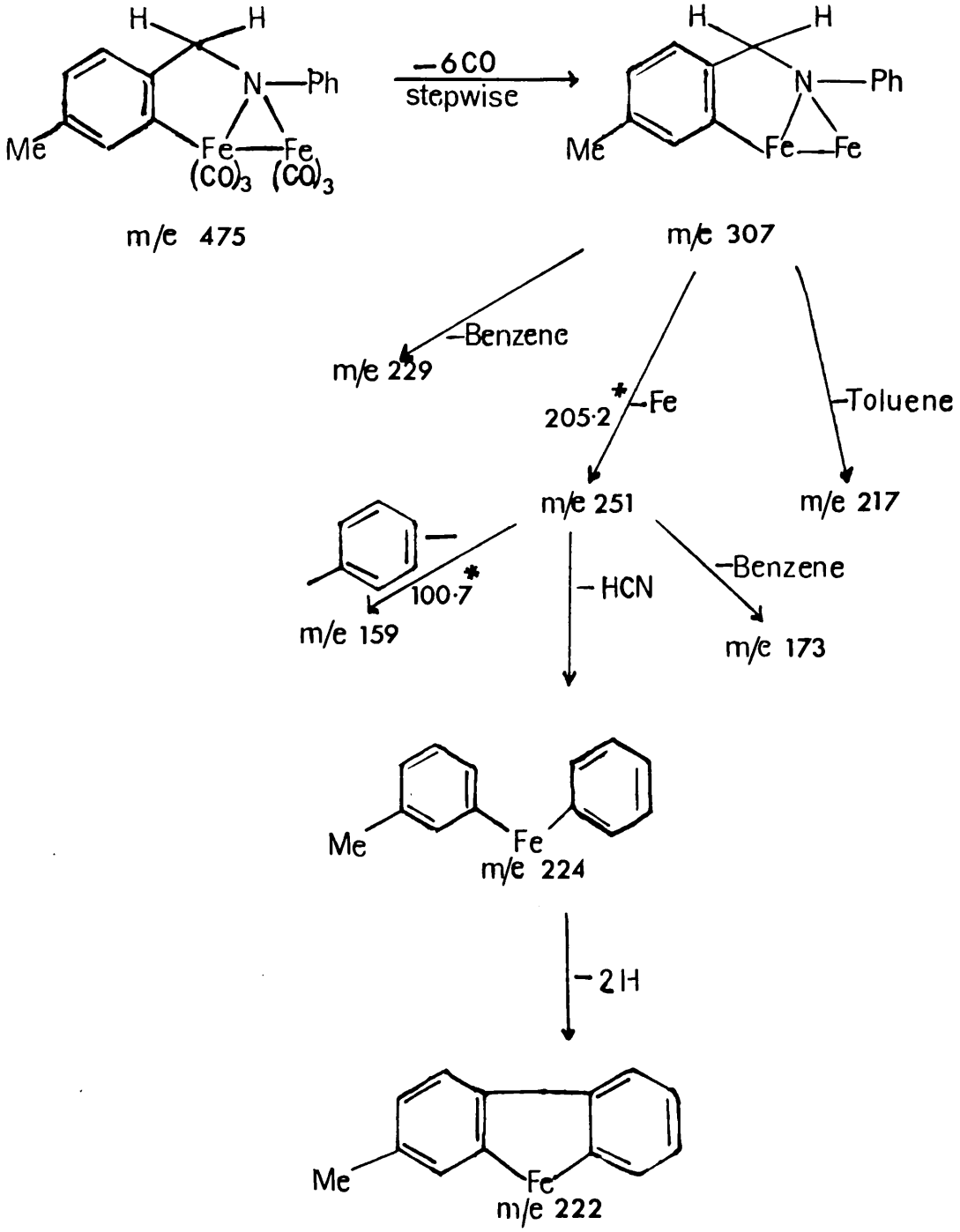


Fig. 27

followed by loss or iron to give the ion m/e 251, and in the case of XVIe elimination of benzene to yield m/e 229. What was surprising, however, was that fragmentation of the ion m/e 251 gave identical products in the ions m/e 224, 222, 173 and 159. M/e 224 and 222, of course, could be rationalised as elimination of hydrogen cyanide from the $(P - 6CO - Fe)^+$ ion followed by two hydrogens, a process quite familiar already in the benzalaniline complex; whereas the formation of the ions m/e 173 and 159 supported by appropriate metastable ions, could only be formed by elimination of benzene and toluene respectively. In XVIe m/e 159 was the more abundant of the two ions, whilst in XVIf m/e 173 was the major ion. These features were, of course, observed before the labelling studies with D_5 benzaliniline had been carried out and were then difficult to rationalize.

Now, of course, with prior knowledge of the mechanism of loss of benzene from the $(P - 6CO)^+$ and $(P - 6CO - Fe)^+$ ions of the labelled compled it is quite readily seen that the two complexes XVIe and XVIf both fit rigorously with this mechanism.

The mass spectral breakdown of XVIe is shown in Fig. 27.

(c) Complex from Pentafluoro N Benzylidene Aniline (XVIg).

Apart from the breakdown of the parent ion of this complex by successive elimination of carbon monoxide to form m/e 365 (the base peak of the spectrum), further cracking is totally unlike any of the other substituted anils. The $(P - 6CO)^+$ is exceptionally stable and shows very little fragmentation. Ions of very low abundance, however, are to be found which correspond to successive removal of all four fluorine atoms, and except for ions corresponding to decomposition of the uncomplexed ligand, this amounts to the total fragmentation exhibited by the complex.

(iii) Nature of R_3 (XVIh)

The only complex so far prepared other than aryl substituted groups in the R_3 position is that of R_3 = methyl. The preliminary loss of benzene from the $(P - 6CO)^+$ ion observed in the benzalaniline complex is not paralleled by a loss of methane from the methyl substituted complex, nor is thereelimination from the $(P - 6CO - Fe)^+$ ion. Where similarities do occur, however, are in the elimination of hydrogen cyanide from both m/e 231 $(P - 6CO)^+$ and m/e 175 $(P - 6CO - Fe)^+$ to form the ions m/e 204 and m/e 148. The latter process is comparable with the formation of m/e 154 in azobenzene and benzalaniline, the more so since the succeeding process involves elimination of two hydrogens. This is

Complex from Benzylidenemethylamine

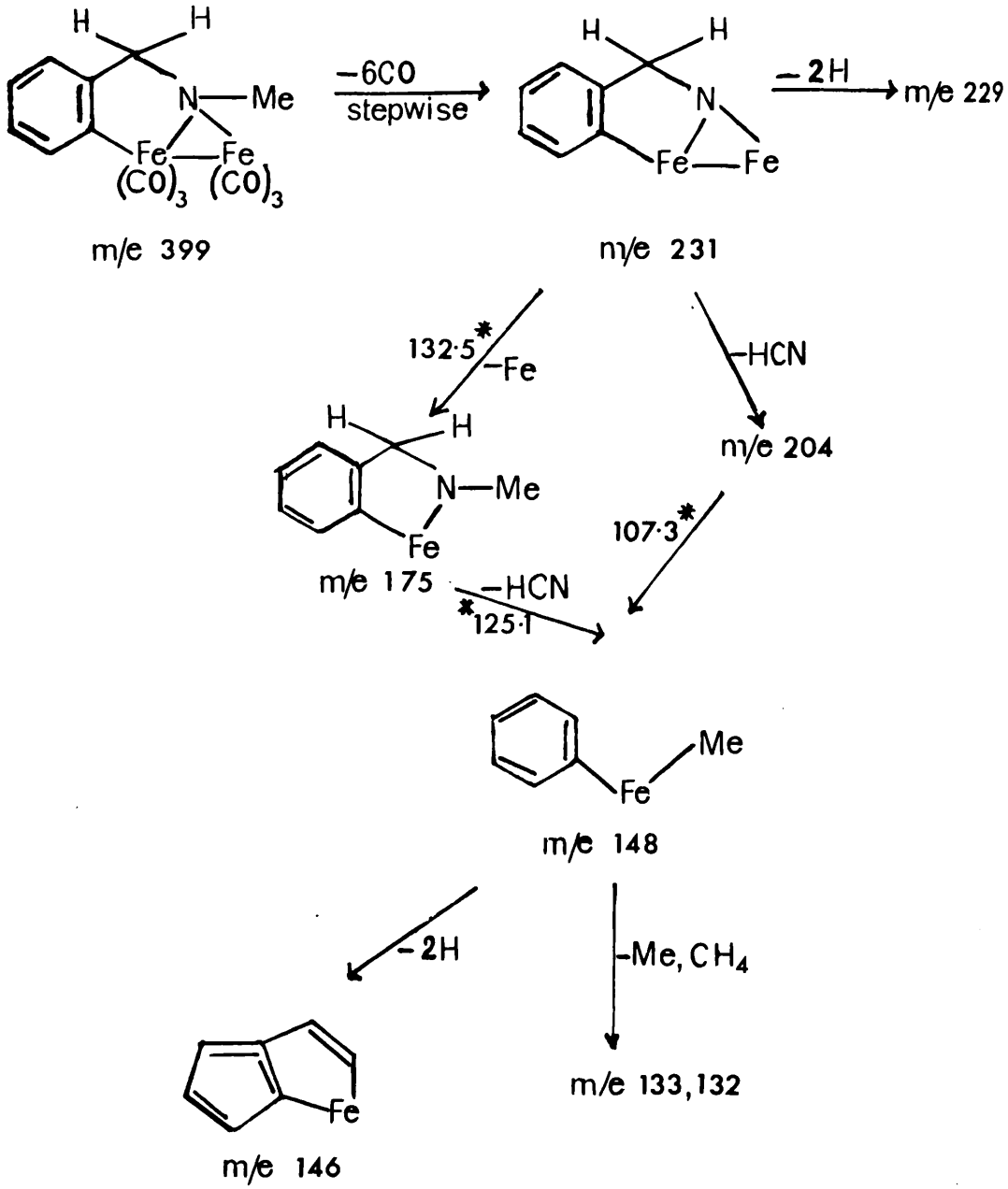


Fig. 28

surprising since benzylidene methylamine itself shows no tendency to eliminate the central hydrogen cyanide molecule, once more amply demonstrating the effect of the metal orbital system upon the nature of decomposition of the organic ligand, and the need to study structure as an entity. The mass spectral breakdown of XVIh is shown in Fig. 28.

Conclusions:

The mass spectra of complexes derived from reactions of substituted azobenzenes, benzophenoneazines, phenyl hydrazones, and benzalanilines with iron carbonyls have shown the existence and structural features of compounds hitherto unreported and novel in constitution. The ability of iron carbonyls to cleave nitrogen - nitrogen bonds and, in some cases, to produce molecular rearrangements within aromatic systems has also been demonstrated. In addition isotopic labelling and mass spectrometry have elucidated the mechanism of formation of metal complexes derived from substituted benzalanilines.

Several weaknesses in the mass spectrometric method of structure determination have been uncovered. Notably in the complex derived from benzophenoneazine and iron enneacarbonyl, reliance on the analogy of existing known rearrangements allowed a misinterpretation of structure to be made, and underlines the great difficulty which ion rearrangements can cause in structural assignments.

EXPERIMENTAL

The mass spectra were determined using an A.E.I. M.S.9 double-focussing mass spectrometer at a source temperature of 180°C and an ionizing voltage of 70eV. A direct inlet system was used to introduce the samples.

The details of experimental methods used to synthesise labelled compounds are shown overleaf, followed by tabulation of the mass spectra of the compounds examined.

The author gratefully acknowledges the co-operation and advice afforded by Professor Pauson, Dr. G.R. Knox, Dr. M.M. Bagga and Mr. W. Flannigan of the University of Strathclyde, Glasgow, during the course of this work.

Preparation of Deuterium Labelled Complexes For Mass Spectral Analysis

Preparation of α-Deutero benzaldehyde

α-Deutero benzaldehyde was prepared according to the method of Bennett, Kirby and Moss (37). Only 66% incorporation of deuterium was obtained as opposed to the 97% value quoted. Correspondence with Prof. Kirby has shown that the last stage in preparation should involve hydrolysis with 4N HCl (aqueous), 1 hour at reflux, and not 2N aqueous/alcoholic HCl as published.

Preparation of α, α, α Trideutero acetophenone

The preparation was carried out according to the method of Noyce, Woodward, and Jorgensen (60). Five exchanges were carried out to give 97.6% α, α, α, trideutero acetophenone by low voltage M.S.

Preparation of N-Benzylidene 2, 3, 4, 5, 6 pentadentero aniline

1.06g (0.01 mole) redistilled benzaldehyde and 1.00g. (0.01 mole) D_7 - aniline (66) were stirred together for 15 minutes. 20 ml of ethanol were then added, cooled in ice and the anil precipitated by dropwise

addition of water. Filtration and recrystallization from ethanol gave N-benzylidene 2, 3, 4, 5, 6 pentadeutero aniline, 91.7% (1.66g). Isotopic Purity 95% D_5 by low voltage M.S.

Preparation of N-(α deutero benzylidene) - 2, 3, 4, 5, 6 pentadeutero aniline

0.7g (0.006 mole) α-deutero benzaldehyde

0.654g (0.006 mole), D_7 - aniline

As for N-Benzylidene 2, 3, 4, 5, 6 pentadeutero aniline. Yield 91% (1.10g) Isotopic Purity 66% D_6, 33% D_5H by low voltage M.S.

α, α, α Trideutero acetophenone anil

2.4g (0.002 mole) of acetophenone - D_3 and 2.738g (0.025 mole) of formamide acetal hydrochloride (67) were stirred in ethanol (7.5 ml) for 4 days gave a 97% yield of D_3 acetophenone diethyl ketal (67b). 2.5g of the ketal were then stirred with 1.2g of aniline - D_2, the ethanol removed by distillation, and α, α, α trideutero acetophenone anil 25% (0.72g). Isotopic Purity CD_3 (12%), CD_2H (23%), CDH_2 (33%), CH_3 (33%).

Mass Spectrum of Complex from Azobenzene.(1V).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	3.6	134	7.9	182	10.1	324	0.9
51	13.7	135	4.2	183	5.0	348	8.6
53	4.3	138	7.7	184	9.4	349	2.4
54	7.9	139	3.2	209	2.6	350	58.3
56	100.0	146	4.3	210	3.4	351	12.9
		146.5	0,5				
57	9.4	147	14.4	211	9.4	352	2.1
		147,5	2.4				
63	3.6	148	2.4	212	2.8	376	0.8
65	4.2	154	4.3	219	0.9	378	3.7
77	13,7	155	4.4	221	9.4	379	1.1
78	5.8	156	10.8	222	2.1	405	0.65
84	10.1	157	1.3	236	7.2	406	13.7
85	7.9	158	3.2	237	2.2	407	3.6
86	3.2	160	8.9	238	52.5	408	0.5
87	20.1	161	7.3	239	8.6	432	4.2
112	14.4	166	2.1	292	12.9	433	1.9
120	2.9	167	8.5	293	7.5	434	29.5
121	5.0	168	2.1	294	100.0	435	7.4
127	6.3	169	3.4	295	18.7	436	2.2
128	5.8	173	8.6	320	8.9	460	0.1
129	3.6	179	1.4	321	1.2	462	0.7(P)
132	6.5	180	3.7	322	53.9	463	0.1
133	13.7	181	15.8	323	10.8		

Mass Spectrum of Complex from p-methoxyazobenzene.(V1).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	13.1	108	70.3	186	1.4	332	4.9
51	21.3	109	7.0	196	5.4	333	1.8
52	28.9	120	13.8	197	34.4	346	1.5
53	24.8	121	9.7	198	4.9	347	100.0
54	7.6	122	6.9	211	10.3	348	32.4
62	10.3	123	93.8	212	5.7	249	4.9
63	24.8	124	8.6	239	0.7	361	8.3
64	24.1	126	14.1	240	96.5	362	1.4
65	33.1	127	3.4	241	27.7	373	0.7
66	6.7	135	10.3	242	14.5	374	0.4
74	8.3	136	1.6	2433	2.8	375	2.9
75	8.3	138	5.2	259	8.9	376	0.9
76	8.3	139	4.5	260	1.7	401	0.7
77	42.0	140	6.2	289	2.1	402	0.3
78	31.7	148	3.4	290	0.8	403	13.3
79	10.3	149	2.1	303	2.2	404	4.6
80	72.4	154	3.4	304	8.9	405	0.7
81	8.9	156	1.4	305	2.6	465	0.3
91	11.7	168	1.4	315	1.4	467	8.5
92	33.8	169	26.9	316	0.7	468	1.4
93	7.6	170	3.5	317	4.3	481	0.4
106	6.9	184	2.1	318	2.1	482	0.9
107	34.5	185	9.6	331	0.7	483	0.4

(V1) Cont.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
495	0.55						
496	0.1						
510	0.8						
511	0.4						
536	1.6						
537	0.8						
538	22.8						
539	8.3						
540	2.1						
564	0.2						
565	0.1						
566	3.6						
567	0.9						
594	0.2(P)						
595	0.1						

Mass Spectrum of Complex from o-phenylene diamine.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	8.5	109	15.5	302	10.0		
51	14.1	110	3.8	328	3.0		
52	17.0	134	5.5	329	1.5		
53	16.8	135	23.8	330	16.9		
55	11.0	136	2.9	356	3.8		
60	1.1	144	1.0	357	1.0		
61	1.5	145	4.0	358	16.9(P).		
62	3.0	146	1.0	359	4.4		
63	10.0	160	10.8				
64	10.5	161	2.0				
65	14.0	162	100.0				
66	16.1	189	1.2				
67	11.0	190	4.5				
77	9.0	191	1.4				
78	10.0	216	10.5				
79	7.9	217	2.6				
90	2.8	218	84.0				
91	10.0	219	10.0				
92	5.9	245	1.0				
101	9.0	246	40.0				
102	1.2	247	6.4				
108	16.5	272	3.0				

Mass Spectrum of XlV(c).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	19.0	131	17.0	211	7.5	471	4.1
51	46.3	132	66.2	234	4.2	472	71.1
52	10.3	133	100.0	235	4.8	473	24.6
54	14.3	134	21.1	236	37.1	474	4.8
56	100.0	135	1.36	236.5 237	1.4 6.5	498	2.8
57	8.8	151	2.0	262	3.4	499	1.0
74	4.8	152	9.5	263	1.1	500	15.9
75	5.1	153	7.5	264	21.1	501	5.9
76	10.2	154	4.8	265	3.1	502	1.4
77	47.6	157	3.4	266	100.0	526	0.4
78	15.6	158	4.8	267	28.6	527	0.1
81	9.5	159	19.7	268	3.5	528	2.7
82	2.0	160	2.7	311	1.3	529	1.2
103	5.4	180	12.9	312	1.1	554	0.5
104	28.5	181	6.1	313	9.5	555	0.2
105	2.7	186	4.1	314	2.7	556	3.1
106	2.5	187	2.1	367	5.6	557	1.7
107	8.8	188	28.9	368	2.0	582	1.3
110	3.4	189	4.1	369	38.1	583	0.4
111	25.1	208	5.4	370	10.2	584	9.2
113	1.4	209	6.9	371	0.9	585	4.1
130	4.1	210	46.9	470	10.3	586	1.1

Mass Spectrum of XlV(c). Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
610	0.5						
611	0.2						
612	3.0						
613	1.6						
614	0.3						
638	0.1						
640	1.6(P).						
641	0.8						

Mass Spectrum of XV(a).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	31.0	91	4.8	128	1.2	178	0.8
51	30.0	92	20.1	131	1.0	180	3.4
52	17.1	93	100.0	132	3.2	181	2.8
53	3.2	94	10.0	133	5.4	182	1.0
54	6.1	95	0•2	134	1.1	201	6.1
55	1.0	102	2.3	145	2.0	202	1.5
56	14.8	103	86.2	146	3.6	203	44.2
57	6.1	104	63.1	147	16.1	204	7.0
60	1.0	105	44.2	148	18.9	205	91.2
61	4.2	106	7.2	149	22.1	206	14.9
62	6.8	107	2.0	150	2.3	207	2.0
63	12.2	110	1.0	158	1.0	222	0.5
64	5.3	111	0.3	159	2.2	223	1.2
65	26.3	112	12.2	160	3.4	224	2.8
66	52.1	113	1.2	168	2.0	225	1.9
67	12.2	119	1.1	169	2.5	226	0.2
74	9.2	120	1.8	170	3.0	251	4.9
75	12.2	121	11.3	171	0.5	252	1.2
76	45.3	122	2.2	174	1.8	279	2.0
77	33.0	125	2.8	175	2.2	280	1.1
78	23.2	126	3.0	176	8.7	281	6.9
79	2.1	127	13.2	177	3.2	282	1.8

Mass Spectrum of XV(a). Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
304	1.2	418	3.8				
305	0.5	419	1.0				
306	15.2	420	25.1				
307	3.2	421	6.0				
308	93.2	422	1.2				
309	23.2	446	1.2				
310	3.0	447	0.2				
311	1.2	448	6.9				
334	4.9	474	1.0				
335	1.2	476	3.2(P).				
336	33.2						
337	6.9						
338	1.0						
362	2.1						
363	0.8						
364	12.8						
365	2.9						
366	1.0						
390	1.1						
391	0.2						
392	4.3						
393	1.2						

Mass Spectrum of XV(b).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	11.2	91	10.8	131	1.1	204	4.9
51	13.2	92	16.3	132	2.8	205	0.8
52	11.1	93	100.0	133	6.9	217	1.9
53	2.4	94	9.9	134	1.2	218	0.4
54	5.0	102	2.1	145	2.0	219	3.0
55	2.2	103	17.2	146	2.2	220	0.5
56	24.1	104	67.2	147	8.2	223	1.2
57	1.2	105	6.8	148	11.0	224	2.2
61	2.9	106	4.0	149	1.2	225	1.7
62	4.0	110	1.9	167	2.2	226	0.4
63	7.8	111	0.2	168	3.0	277	1.8
64	3.8	112	8.2	169	3.2	278	0.2
65	22.1	113	1.1	170	1.6	279	11.9
66	37.9	117	2.2	174	2.1	280	3.0
67	3.0	118	10.0	175	3.9	281	79.8
74	4.2	119	44.0	176	5.4	282	14.2
75	3.6	120	11.1	177	1.9	283	2.0
76	9.1	121	9.0	180	2.0	320	11.9
77	25.4	125	1.8	181	1.9	321	3.2
78	16.2	126	3.0	201	5.1	322	98.2
79	2.1	127	8.2	202	1.4	323	20.8
90	2.1	128	1.0	203	33.0	324	2.3

Mass Spectrum of XV(b),Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
348	4.2	464	0.5				
349	1.2	488	0.4				
350	28.9	489	0.1				
351	6.9	490	2.5(P).				
352	1.1	491	0.6				
376	1.5	492	0.2				
377	1.5						
378	7.5						
379	1.9						
404	1.2						
405	0.3						
406	4.1						
407	0.9						
432	2.9						
433	0.5						
434	16,5						
435	4.1						
436	1.0						
460	1.2						
461	0.3						
462	0.3						
463	2.1						

Mass Spectrum of (XV11).

M/e	%Abund.	M/e	%Abund,	M/e	%Abund.	M/e	%Abund.
50	5.1	104	22.0				
51	15.8	105	6.0				
52	2.8	151	1.6				
55	1.9	152	5.2				
56	1.1	153	1.8				
57	1.5	178	1.4				
58	5.3	179	2.1				
62	2.0	180	25.0				
63	6.7	181	18.0				
64	3,6	182	2.9				
65	1.5	208	41.5				
74	1.8	209	100.0(P).				
75	2.6	210	20.0				
76	7.4	211	2.2				
77	48.0						
78	13.0						
79	1.4						
89	9.2						
90	8.1						
91	2.0						
102	1.3						
103	1.9						

Mass Spectrum of XVl(a).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	6.0	110	1.6	216	1.2	403	2.8
51	30.8	112	28.4	234	8.8	404	0.8
54	9.2	132	29.6	235	35.0.	405	19.6
56	60.0	133	11.6	236	9.6	406	4.8
57	12.4	134	9.6	237	100.0	431	0.4
63	6.0	146.5	24.0	238	17.6	433	1.2
65	5.2	152	12.0	239	2.0	434	0.4
76	4.0	153	6.0	291	17.6	459	1.2
77	39.6	157	4.0	292	4.0	461	8.0(P).
78	8.8	158	2.3	293	96.0	462	2.4
81	12.4	159	20.4	294	22.2		
82	4.8	160	3.2	319	8.4		
84	16.0	179	6.0	320	1.6		
89	8.0	180	38.0	321	60.0		
89.5	1.0						
90	2.8	181	30.0	322	12.8		
90.5	1.2						
91	13.6	182	7.2	347	5.4		
93	2.0	183	6.8	348	1.8		
94	5.6	208	6.8	349	35.6		
95	2.0	209	5.2	350	9.3		
103	2.0	210	14.8	375	0.4		
104	6.0	211	3.2	377	2.0		
105	4.0	215	7.4	378	0.5		

Mass Spectrum of XV1(b).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	12.2	104	17.1	152	8.1	210	4.1
51	66.2	105	20.5	153	1.2	211	0.5
52	8.0	106	2.8	179	2.8	227	1.2
53	2.1	111	1.3	180	100.0	228	0.2
54	1.8	112	6.2	181	37.2	229	6.3
55	1.0	117	2.1	182	19.1	230	1.4
56	15.2	118	31.2	183	3.1	249	2.1
57	1.6	119	4.1	193	4.8	250	1.0
62	2.2	120	2.2	194	8.1	251	7.9
63	7.2	121	3.2	195	93.1	252	1.8
64	3.0	122	0.8	196	24.9	264	0.5
65	7.0	131	0.8	197	15.0	266	2.0
66	4.8	132	5.9	198	3.0	267	0.3
67	1.0	133	5.0	201	2.0	279	0.7
74	3.0	134	1.2	202	1.0	280	0.4
75	4.0	145	1.1	203	8.9	281	3.3
76	12.2	146	1.8	204	1.5	282	0.7
77	92.2	147	4.8	205	4.1	305	9.1
78	22.7	148	2.1	206	0.9	306	3.1
79	4.8	149	1.3	207	0.2	307	65.2
102	3.2	150	1.00	208	1.8	308	13.0
103	14.2	151	2.9	209	2.0	309	2.1

Mass Spectrum of XVl(b). Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
333	5.2	448	0.3				
334	1.6	449	0.1				
335	41.2	473	0.9				
336	9.5	474	0.2				
337	2.1	475	6.9(P).				
361	3.0	476	1.8				
362	1.0	477	0.4				
363	19.9						
364	4.8						
365	1.5						
389	1.6						
390	0.5						
391	11.1						
392	2.9						
393	0.8						
417	3.8						
418	1.0						
419	24.3						
420	6.2						
421	1.8						
445	0.2						
447	0.9						

Mass Spectrum of XVl(c).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	6.0	148	6.0	370	25.0		
51	36.5	152	12.5	371	4.5		
52	4.5	153	7.0	425	17.0		
56	30.0	154	2.5	426	5.0		
62	1.4	165	66.0	453	26.0		
63	5.0	166	19.5	481	15.0		
67	3.0	167	23.0	537	1.6(P).		
77	31.0	168	10.0				
78	12.0	179	2.8				
81	2.4	180	100.0				
89	2.7	185	7.0				
91	3.0	254	7.5				
93	9.5	256	30.5				
103	2.0	257	77.5				
104	2.5	258	16.0				
112	7.0	259	7.0				
115	3.7	292	4.0				
121	4.0	296	2.5				
130	8.0	367	15.0				
137	4.0	368	8.5				
147	3.5	369	100.0				

Mass Spectrum of XV1(d).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	15.0	91	22.3	172	8.9	235	44.2
		91.5	0.5	173	2.9		
51	53.2	103	8.2	174	3.2	236	14.1
52	10.1	104	37.2	175	0.8	237	4.0
53	1.1	105	7.0	179	2.9	268	1.2
54	3.9	106	33.0	180	100.0	269	2.0
55	1.9	107	2.0	181	38.2	270	5.1
56	55.6	125	27.8	182	20.2	271	6.0
57	4.0	126	3.7	183	3.1	272	3.0
62	3.9	127	9.6	207	1.2	273	2.3
63	3.9	128	3.0	208	4.5	300	2.3
64	5.1	129	0.5	209	7.2	301	1.5
65	11.6	130	1.6	210	4.1	302	1.1
66	7.8	131	4.0	211	1.0	325	15.2
67	3.0	132	7.3	213	1.8	326	3.8
76	7.0	133	8.6	214	29.5	327	47.1
77	96.2	134	1.6	215	34.0	328	16.8
78	32.8	151	5.9	216	19.2	329	28.0
79	3.2	152	20.8	217	28.2	330	5.2
80	0.2	153	8.9	218	5.9	353	7.0
81	8.2	154	3.9	232	2.0	354	1.5
89	17.8	163	2.6	233	2.0	355	55.2
89.5	6.0	163.5	14.2				
90	11.3	164	3.0	234	15.2	356	11.1
90.5	9.0	164.5	4.8				

Mass Spectrum of XVl(d) (Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
357	18.2	469	1.8				
358	3.9	493	1.5				
381	4.2	494	0.5				
382	1.0	495	8.2(P).				
383	32.1	496	2.1				
384	7.5	497	3.0				
385	11.8	498	0.8				
386	2.5						
409	0.4						
411	3.0						
412	0.7						
413	1.2						
437	4.5						
438	1.1						
439	33.8						
440	7.9						
441	11.2						
442	2.1						
465	1.0						
466	0.3						
467	4.0						
468	1.2						

Mass Spectrum of XV1(e).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	4.2	76	2.9	98	0.4	129	0.4
51	21.4	77	61.5	101	0.4	130	0.3
52	3.5	78	10.5	102	1.1	131	0.4
53	1.2	79	3.0	103	4.1	132	0.9
54	1.1	80	0.3	104	13.0	133	0.8
55	1.2	81	0.8	105	39.0	134	1.0
56	5.1	82	0.5	106	6.9	137	0.6
57	1.6	83	0.7	107	0.5	138	0.5
		83.5	4.2				
61	0.3	84	0.8	112	2.9	138	0.5
62	1.1	85	0.3	113	0.3	139	0.6
63	4.2	86	0.3	114	0.3	140	0.4
64	1.7	87	0.4	115	1.1	141	0.6
65	8.0	88	0.4	116	2.5	146	2.3
66	2.4	89	4.0	117	1.9	147	0.6
67	0.5	90	3.3	118	2.0	148	1.3
68	0.2	91	19.6	119	0.8	151	0.8
69	0.7	92	7.6	120	0.4	152	1.8
70	0.2	93	8.3	121	0.5	153	1.0
						153.5	10.1
71	0.5	94	0.6	125	1.6	154	1.8
73	0.2	95	0.4	126	0.4	159	1.7
		95.5	2.3				
74	1.2	96	0.2	127	0.8	160	0.4
		96.5	8.0				
75	1.5	97	14.3	128	0.7	161	0.3

Mass Spectrum of XVl(e).Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
162	0.4	195	88.0	252	2.6	475	0.5
163	0.5	196	22.0	253	0.3	476	0.1
164	0.4	197	19.4	254	0.2	477	3.2(P).
165	3.2	198	2.6	303	0.2	478	0.8
166	1.8	199	0.3	304	0.5		
167	1.6	200	0.2	305	6.0		
168	0.9	213	0.2	306	1.5		
171	0.3	214	0.3	307	40.0		
172	0.2	215	0.7	308	8.5		
173	1.2	216	0.5	309	1.1		
174	0.6	217	1.3	333	2.8		
178	1.6	218	0.4	334	1.1		
179	2.0	219	0.9	335	23.0		
180	7.0	222	0.9	336	4.8		
181	2.8	223	0.5	337	0.8		
182	1.5	224	2.1	417	1.4		
183	0.9	225	0.5	418	0.4		
190	0.5	247	0.5	419	12.0		
191	1.0	248	0.9	420	2.7		
192	1.7	249	3.9	421	0.6		
193	5.4	250	1.1	447	0.7		
194	100.0	251	15.5	448	0.2		

Mass Spectrum of XVl(g).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
50	11.0	234	31.0	477	11.5		
51	36.5	235	39.0	505	1.1		
52	8.5	236	7.5	533	2.8		
65	16.5	237	5.5				
66	9.0	251	3.3				
77	100.0	252	27.0				
78	13.0	253	48.0				
92	14.0	254	17.5				
93	20.0	255	32.0				
99	4.3	256	4.7				
103	3.5	270	30.0				
104	32.5	288	1.7				
105	7.3	289	2.1				
106	18.0	290	1.5				
143	5.6	363	3.7				
145	7.8	364	0.2				
150	5.5	365	30.0				
163	29.0	390	1.6				
176	4.5	393	14.0				
177	5.4	394	2.6				
216	4.6	421	6.5				
217	5.0	449	2.7				

Mass Spectrum of XVl(h).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abumd.
50	15.1	89	8.9	136	2.0	228	1.2
51	28.3	90	7.2	137	3.2	229	27.6
52	8.0	91	67.1	138	1.8	230	4.1
53	2.2	92	7.8	146	7.0	231	64.1
54	3.0	97	4.8	147	1.8	232	9.1
55	1.2	102	1.8	148	25.7	233	1.1
61	2.1	103	12.0	149	2.7	257	11.1
62	5.2	104	5,8	153	1.2	258	1.9
63	12.7	110	4.1	173	4.3	259	83.1
64	4.0	111	0.2	174	3.8	260	10.9
65	13.4	112	31.2	175	15.1	261	1.5
66	2.2	113	3.1	176	2.0	285	3.0
75	4.6	117	9.9	187	0.5	285	3.0
76	9.9	118	100.0	188	0.8	286	0.8
77	45.3	119	94.3	189	0.2	287	28.1
78	35.3	120	22.3	200	1.2	288	4.9
79	3.2	121	4.1	201	0.7	289	1.0
81	4.3	131	1.2	202	2.5	313	1.2
82	1.8	132	8.8	203	1.0	314	0.3
83	2.0	133	5.2	204	3.5	315	9.0
84	4.8	134	2.1	205	1.0	316	2.0
85	1.0	135	0.2	227	5.1	397	2.9

Mass Spectrum of XVl(h).Cont'd.

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
398	1.0						
399	21.2(P).						
400	5.0						

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Appendix to Chapter Two

The ways in which the nature of a particular ligand system affect the electronic energy levels of a metal ion have been studied in three main directions (1). These are as follows:-

(i) The electrostatic crystal field theory first developed by Bethe (2), which is unsuitable for many classes of complex, and assumes that all interactions between the metal ion and its surroundings may be treated as purely electrostatic effects between point charges.

(ii) The fundamental molecular orbital theory which assumes all bonding results from an overlapping of the orbitals of the metal with the appropriate symmetry orbitals arising from a linear combination of the ligand molecular orbitals.

(iii) The ligand field theory which uses the symmetry considerations of Bethe's method but combines with the electrostatic approach one which allows the existence of chemical bonding between the metal ion and the ligand system.

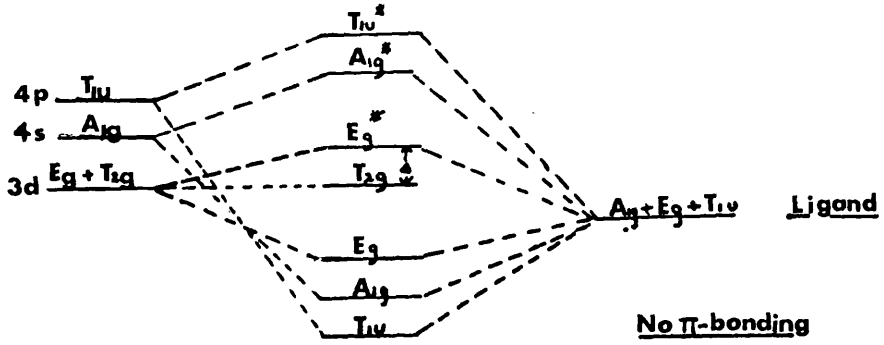
It is useful here to show how the molecular orbital approach can be applied to obtain a set of energy

levels in a metal complex. Firstly one must determine which orbital overlaps are, and are not, possible because of the inherent symmetry requirements of the problem. This method is most easily applied in octahedral complexes, which we shall now consider.

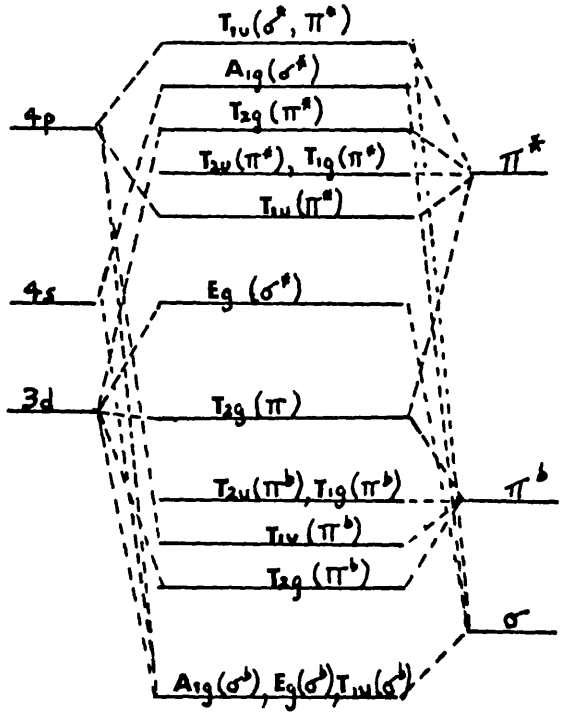
In complexes of metals of the first transition series the molecular orbitals most commonly used in bonding with ligands are the 4s, 4p and 3d orbitals. Assuming that each ligand of the six in an octahedral system possesses one σ orbital, these must be combined into six "symmetry" orbitals, each constructed so as to "overlap" with a particular one of the six orbitals in the metal which are available for σ - bonding. If, in addition, the ligands also possess π orbitals these too must be combined so as to overlap effectively with the metal ion π orbitals.

For complexes without π overlap the six σ symmetry orbitals are the A_{1g} (s), E_g (d_{z^2}, $d_{x^2-y^2}$), and T_{1u}(p_x, p_y and p_z) orbitals. A_{1g} represents a single orbital which has the full symmetry of the molecular system, E_g represents a pair of orbitals which are equivalent except for their orientations in space. The final step is to allow each metal orbital to overlap with the appropriate symmetry orbital of the ligand system.

a,



b.



Metal Hexacarbonyl

Fig 1

Two combinations are to be considered: one in which the matched orbitals unite with maximum positive overlap, thus giving a bonding molecular orbital and the other in which they unite with maximum negative overlap to give the corresponding antibonding molecular orbital. The molecular orbitals of the same symmetry class which differ only in orientation have the same energies, whereas orbitals of different symmetry classes do not. The energy level diagram for purely σ bonded octahedral complexes is shown in Fig 1(a).

Generally speaking, in diagrams of this type, it may be assumed that if a molecular orbital is much nearer in energy to one of the atomic orbitals used to construct it than the other, it has much more the character of the first than the second. On this basis, therefore, the six bonding molecular orbitals, namely three T_{1u}, the A_{1g} and two E_g have more ligand character than they have metal character. It can then be said that electrons occupying these orbitals will be mainly "ligand electrons" rather than "metal electrons", though they will possess significant metal ion character. Conversely electrons occupying any of the T_{2g} orbitals are to be considered as predominantly metal electrons.

If the ligands possess π orbitals, filled or unfilled, it is necessary to consider their interactions with the T_{2g} d orbitals, i.e. d_{xy}, d_{yz}, and d_{zx} orbitals. The effects of π bonding through orbitals of symmetry T_{2g} must now be considered. These effects will vary depending on the energy of the orbitals of the ligand relative to the energy of the T_{2g} orbitals of the metal and the extent to which the π orbitals of the ligand are filled.

Where there are empty π orbitals of higher energy than the T_{2g} system of the metal, the result is to stabilize (i.e. lower the energy) the metal T_{2g} orbitals relative to the E_g^* orbitals, acquiring some ligand character in the process. Where there are orbitals of lower energy than the T_{2g} orbitals of the metal, the interaction raises the energy of the T_{2g} orbitals relative to the E_g^* system.

Thus in metal carbonyl bonding there is competitive interaction between the antibonding (π^*) and bonding (π^b) orbitals of the carbonyl ligand and further the degree to which the metal T_{2g} orbitals assume ligand character is a function of the extent of the interaction between the π^* ligand and T_{2g} molecular orbitals.

Fig. 1(b) shows the energy diagram which has been calculated for the complex $Cr(CO)_6$(3). The pure π molecular orbitals are composed of the d_{xy}, d_{xz} and d_{yz} metal orbitals and the T_{2g} combinations of π^b and π^* ligand molecular orbitals. The combining orbitals in order of decreasing stability is always π^b (ligand), $d\pi$ (metal), and π^* (ligand). Thus there are formed three (degenerate) π molecular orbitals mainly localized on the carbonyls; three weakly bonding (or non-bonding) π molecular orbitals formed by overlap of the π^* and T_{2g} orbitals mainly localized on the metal; and three strongly antibonding molecular orbitals mainly localized on the carbonyls.

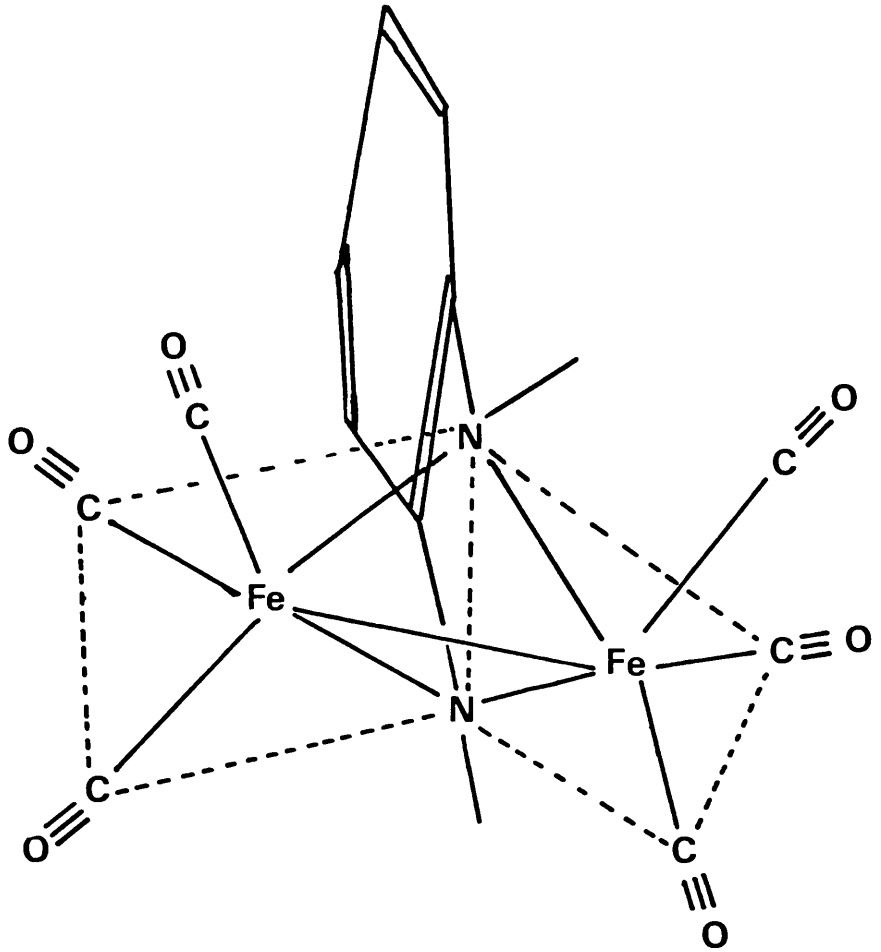
The transition from consideration of a purely octahedral all - carbonyl system to structures of the type (LL^1) $Fe_2(CO)_6$ which have been the main consideration of Chapter 2 is quantitatively very difficult and at this stage no full energy diagram can be drawn for these systems. The main symmetry class(C_{2v}) is now much lower but the basic principles developed in the preceeding dicussion will hold good. Both iron atoms in these complexes are in an S^2d^6 state and hence the six orbitals of T_{2g} symmetry, although not necessarily degenerate con contain all twelve d electrons. If we then consider the primary

ionization process to take place by removal of one electron from the highest occupied molecular orbital then the synergic nature of π bonding between the π^* orbitals of the carbonyl ligands and the metal T_{2g} orbitals will be disrupted. This idea has been substantiated in the octahedral $Cr(CO)_6$ system (4) and very recently has shown to be valid in non octahedral systems containing phosphorus and carbonyl ligands (5).

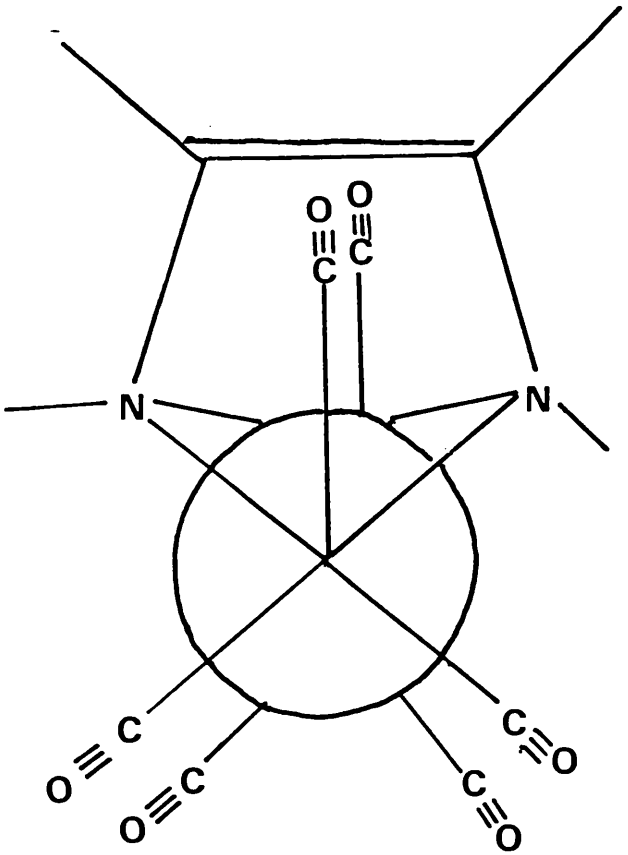
The stability of the parent ion formed, therefore, will be dependent on how successfully the metal T_{2g} orbitals can stabilize themselves. It is likely, however, that the already weakly bonding T_{2g} orbital system will become partially antibonding and cause destabilization of the metal-carbonyl molecular orbital system. This is presumably the reason why carbonyl ligands are eliminated preferentially in the electron impact induced dissociation in these systems.

It can, therefore, be seen that successive elimination of carbon monoxide from the molecular ion will be followed by rearrangement of energy levels within the molecular orbital system in order that maximum orbital overlap of all ligands and the metal ion occur, i.e. the system will change shape. The nature of these processes will obviously be dependent upon the bonding

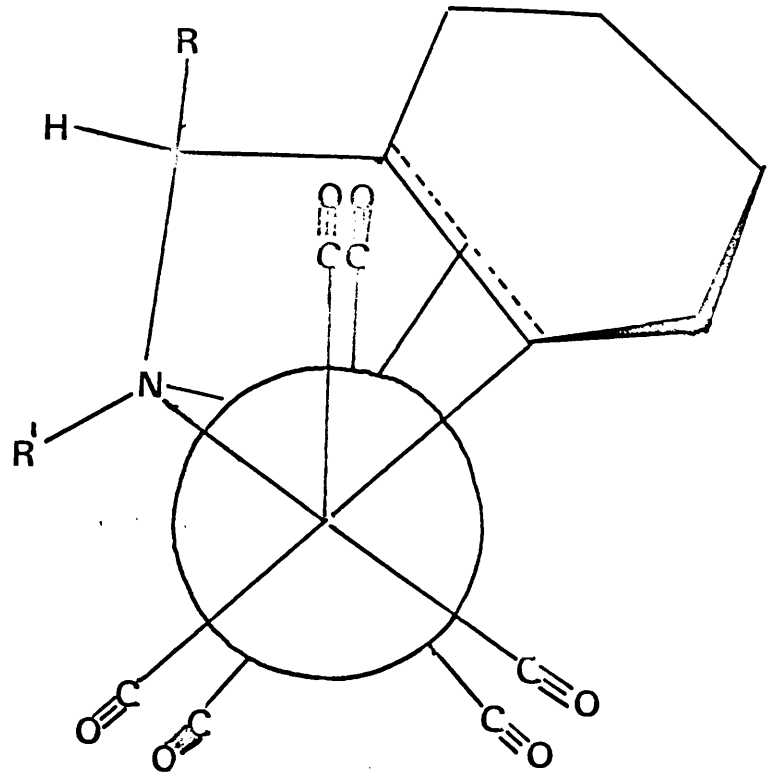
o-Semidene Complex



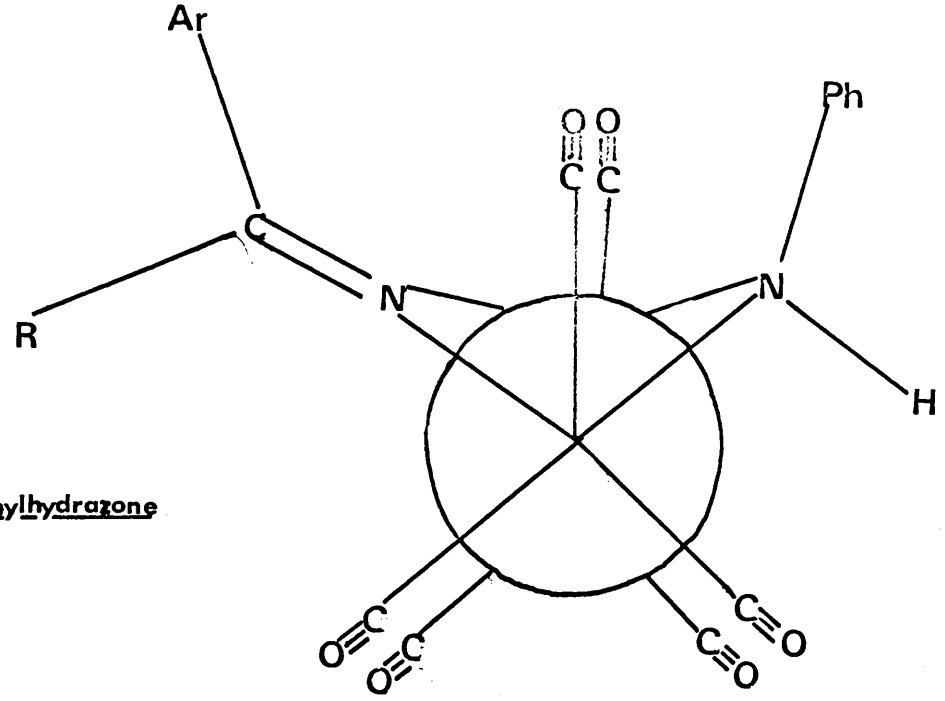
Pictorial view



View along the Fe-Fe bond



Benzalaniline



Phenylhydrazone

characteristics of L^1 and L with the metal ion, and hence the stabilities of the fragment ions formed during these successive eliminations will be dependent upon the nature of L and L^1 and the energy of the ionizing electrons.

It has been shown that the σ donor abilities of a series of ligands have a marked effect on the ionization potential of the metal carbonyl or nitrosyl complexes derived from them (5) and in consideration together with the theory postulated above it seemed likely that a variation in the nature of L and L^1 would produce recognisable changes in the abundances of the ions derived from successive elimination of carbon monoxide from the parent ion.

It was, therefore, decided to study the mass spectral decomposition of the various substituted complexes of o - semidenes, benzalanilines and phenyl hydrazones which were of the type $(LL^1)\ Fe_2(CO)_6$, more closely. Structural diagrams of these complexes are shown opposite. It will be noted that only in the o - semidene case is the complex of true C_{2v} symmetry ($L = L^1$) and the only π bonds which are present in the complex are those of the metal carbonyl systems. All other bonding takes place through σ orbitals. In

benzalaniline, however, an intrinsic part of the ligand bonding is the participation of the π system of the benzene ring and in the phenyl hydrazone complexes although the majority of bonding with L and L^1 occurs by σ bonding through the nitrogen atoms it is possible that some interaction takes place between the π or π^* orbitals of the sp^2 hybridised nitrogen.

It has already been stated that the complexes of the type $(LL^1)\ Fe_2(CO)_6$ lose the metal carbonyl groups in a consecutive manner upon electron impact. What became immediately obvious when a large number of spectra of a particular structural type had been studied was the fact that the abundancies of the parent ion and those ions corresponding to the successive elimination of carbon monoxide demonstrated a remarkable similarity to one another yet differed from the ion abundancies encountered in the fragmentation of other structural types. Thus complexes derived from substituted benzalanilines showed features similar to one another yet differed from those complexes derived from substituted o - semidenes and phenylhydrazones.

It was found, for example, that if the section of the mass spectrum from the parent ion (^{56}Fe monoisotopic) down to the $(P - 6CO)^+$ ion was considered apart from the rest of the spectrum, and if abundancies of these ions

(a_m) were expressed in terms of percentage total ionization within the section (Σa_m) then graphs of $a_m/\Sigma a_m$ ("A") against the number of carbonyl groups lost (m) gave a "fingerprint" of the particular ligand type.

Table 1 shows a comparison of "A" values at 70eV for the parent and fragment ions(m) for ten related benzalaniline complexes. Mean values have also been calculated and standard deviations found as shown in Table 2.

Table 1

	$a_m/\Sigma a_m \times 10^2$						
Complex	P^+	$(P-CO)^+$	$(P-2CO)^+$	$(P-3CO)^+$	$(P-4CO)^+$	$(P-5CO)^+$	$(P-6CO)^+$
1. $R_1=C_6H_4, R_2=H, R_3=C_6H_5$.	3.7	0.5	11.2	6.9	11.5	23.0	44.0
2. $R_1=C_6H_4, R_2=H, R_3=C_6D_5$	3.6	0.5	11.2	7.0	11.5	22.8	43.1
3. $R_1=C_6H_4, R_2=CH_3$ $R_3=C_6H_5$.	3.8	0.7	15.2	6.8	12.5	25.7	41.2
4. $R_1=pMeC_6H_3, R_2=H$ $R_3=C_6H_5$.	3.7	0.7	16.1	6.6	10.7	24.4	42.0
5. $R=C_6H_4, R_2=H$ $R_3=C_6H_4pMe$	3.9	0.7	10.1	9.60	10.6	24.8	40.0.
6. $R_1=oCl\ C_6H_3$, $R_2=H, R_3=C_6H_5$	3.5	(1.5)	14.7	(1.3)	14.2	24.3	39.2
7. $R_1=C_6F_4, R_2=H$ $R_2=C_6H_5$.	3.8	(1.4)	15.0	4.9	11.0	20.0	43.5
8. $R_1=C_6H_4, R_2=C_6H_5$ $R_3=C_6H_5$.	(1.0)	0.20	7.4	5.7	9.1	24.3	(52.9)
9. $R_1=C_4H_2S$, $R_2=H, R_3=C_6H_5$.	3.4	(2.5)	14.2	4.6	8.4	27.1	39.7
10. $R_1=C_6H_4, R_2=H$, $R_3=Me$	(4.8)	0.80	13.5	(3.2)	10.5	27.4	39.8

Table 2

(a) Mean values of "A" for complexes 1 → 10

m	Mean A
P^+	3.5 ± 0.9
$(P - CO)^+$	0.9 ± 0.6
$(P - 2CO)^+$	12.8 ± 2.7
$(P - 3CO)^+$	5.7 ± 1.7
$(P - 4CO)^+$	10.9 ± 1.6
$(P - 5CO)^+$	24.4 ± 2.2
$(P - 6CO)^+$	42.4 ± 4.19

(b) Mean values of "A" for complexes 1→ 5

m	Mean A
P^+	3.7 ± 0.04
$(P - CO)^+$	0.6 ± 0.1
$(P - 2CO)^+$	12.8 ± 2.6
$(P - 3CO)^+$	7.4 ± 0.4
$(P - 4CO)^+$	11.3 ± 0.7
$(P - 5CO)^+$	24.1 ± 1.2
$(P - 6CO)^+$	42.1 ± 1.6

In order to make these observations valid, all spectra were recorded at an ion source temperature of 150°C and a constant † monitor reading. In general, each observation of peak height was consistent within ± 5% except in the $(P - CO)^+$ ion, which is of very low intensity and gave variations as much as ± 10%.

It is worthwhile noting that in the compounds

studied great variation in the nature of R_1, R_2 and R_3: occurs (see XVI Chap. 2) and it would, therefore, be expected that any substituents which are likely to cause a change in the nature of the molecular orbital system of the complex would cause a change in the abundancies of the ions under consideration as compared with the standard benzalaniline complex spectrum. Some variation does occur (results in brackets) but it is apparent that the general characteristics of the spectra do not change. The "A" value of parent ions is remarkably constant except for R_2 = Ph and R_3 = Me; minima do occur in all cases at the $(P - CO)^+$ and $(P - 3CO)^+$ ions with an intervening maximum at $(P - 2CO)^+$. The remaining three ions increase in intensity to a maximum at $(P - 6CO)^+$.

It is useful to view the problem also in terms of those substituents which are least likely to affect the metal - ligand orbital system by inductive and mesomeric effects, therefore complexes 1 - 5 were selected. Complex 6 was omitted as it had been observed that multiple losses of carbon monoxide could occur in the dissociation process which was reflected in the abnormally low minimum of the $(P - 3CO)^+$ ion. Calculations on the standard deviations from the mean

Fig. A 70 e.v.

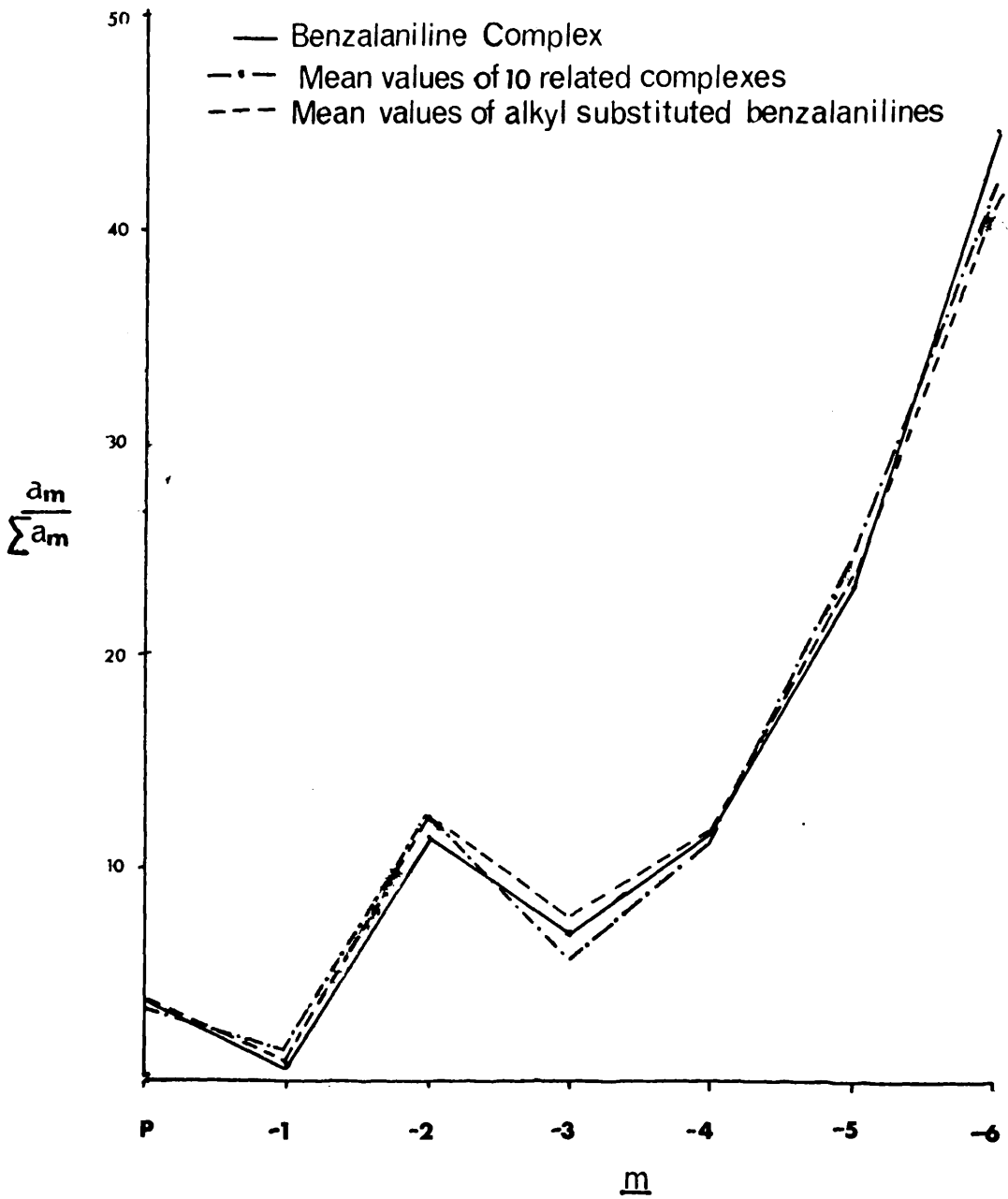

Benzalaniline Complex
Mean values of 10 related complexes
Mean values of alkyl substituted benzalanilines
50
40
30
20
10
$\frac{a_m}{\sum a_m}$
P
-1
-2
-3
-4
-5
-6
m

Fig B 20ev

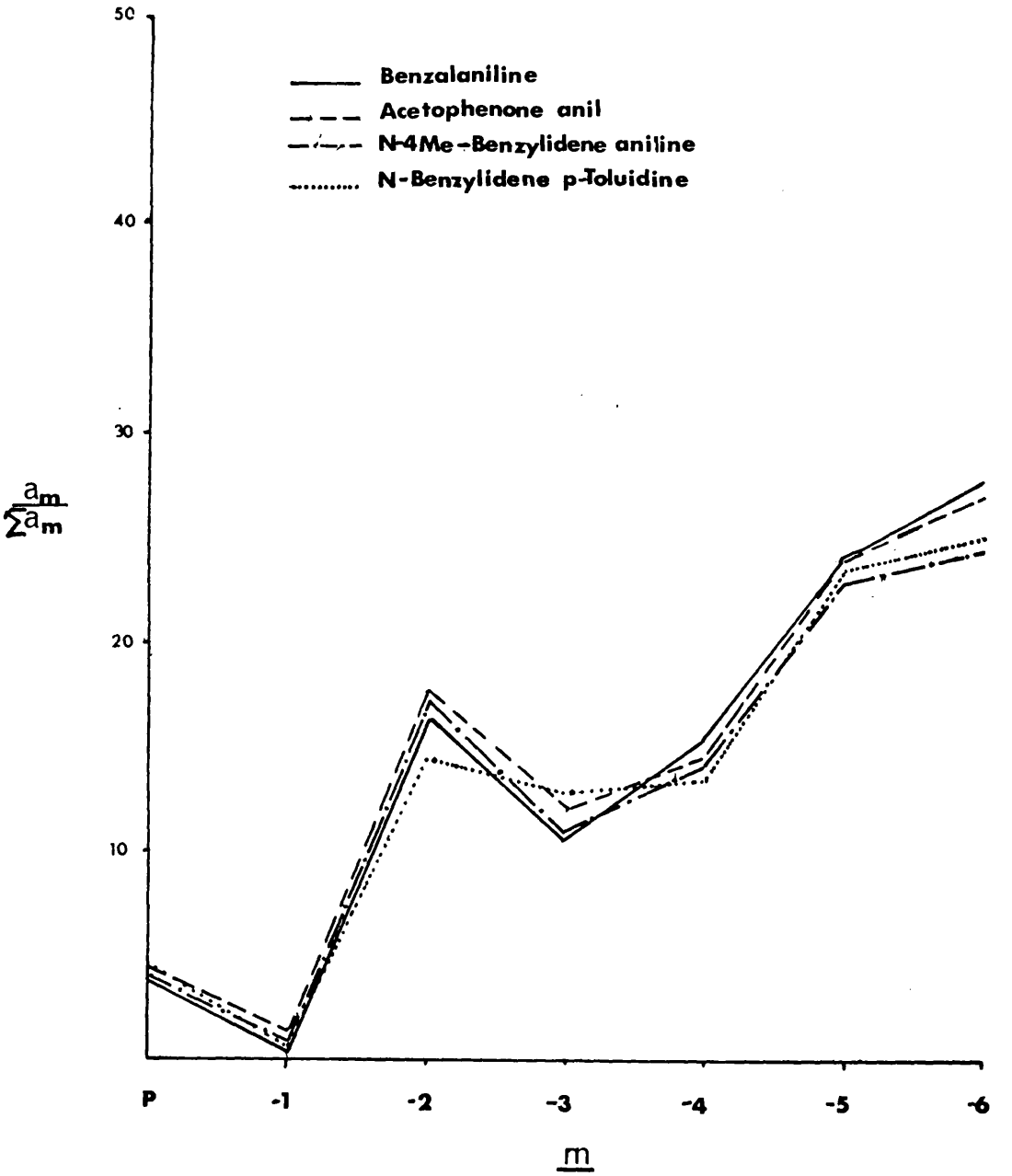
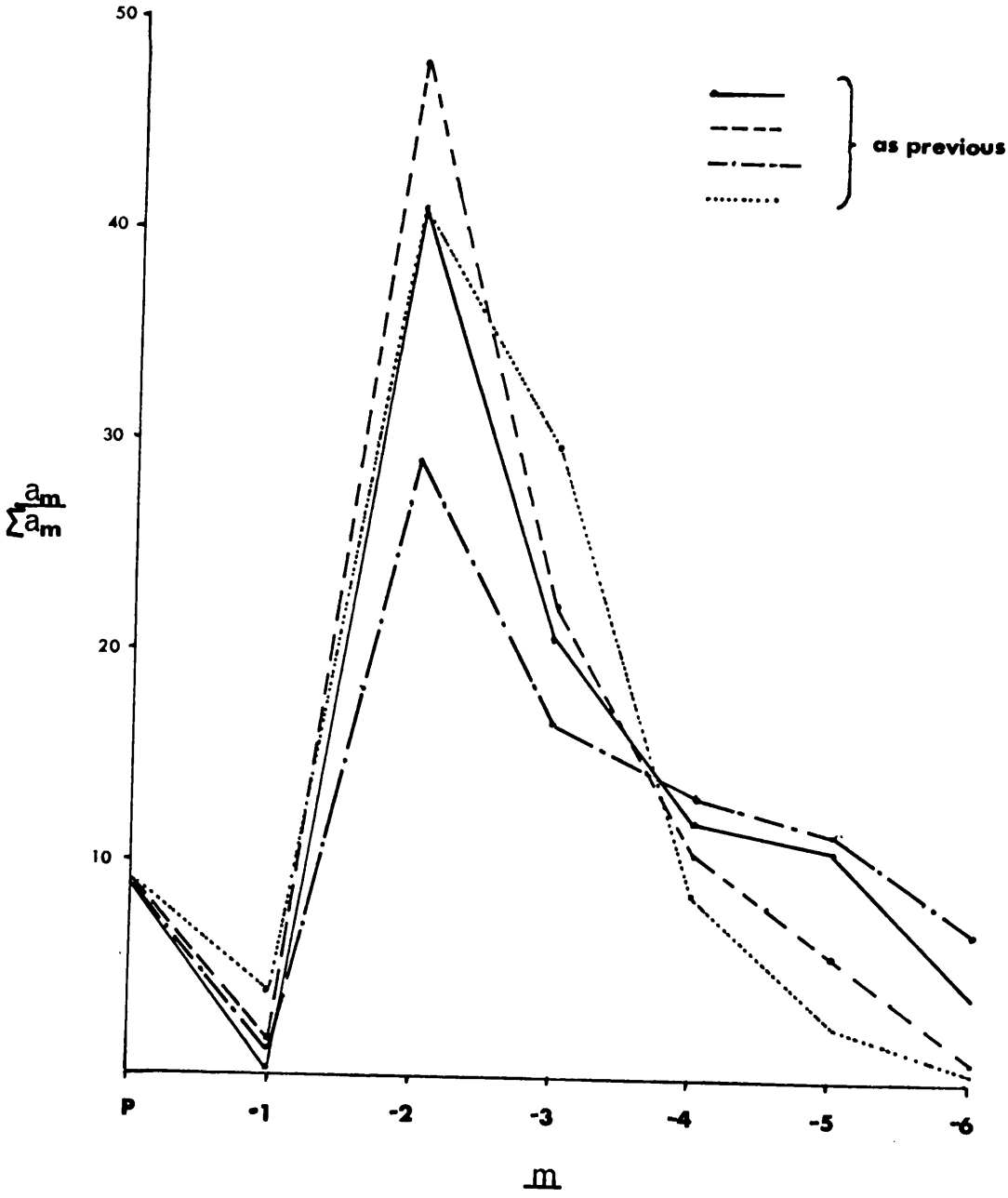

50
40
30
20
10
Benzalaniline
Acetophenone anil
N-4Me-Benzylidene aniline
N-Benzylidene p-Toluidine
$\frac{a_m}{\sum a_m}$
P
-1
-2
-3
-4
-5
-6
m

Fig C 12ev



values showed remarkably good agreement as in Table 2. Figure A also shows the graphical comparison of the "standard" complex ($R_1 = C_6H_4$, $R_2 = H$, $R_3 = Ph$) with the mean of 1 - 5 and with the mean values from 1 - 10.

Figures B and C show the results obtained for these complexes at 20 eV and 12 eV respectively. The immediate effect of lowering the electron voltage to 12 eV is to increase the "A" value of the $(P - 2CO)^+$ ion which becomes the base peak of the spectrum. It can easily be seen that elimination of two carbon monoxide groups is energetically a very favourable process. This is "mirrored" in the behaviour of all benzalaniline type complexes.

That the stabilities of the ions corresponding to consecutive elimination of carbon monoxide from $(LL^1)\ Fe_2(CO)_6$ complexes is a function of the ligand type is borne out by the fact that similar experiments with complexes derived from substituted o - semidenes and phenyl hydrazones gave "A" values which were consistent within the structural type yet differed from one another and from those of the benzalaniline complexes.

Figures D, E and F show respectively the results obtained from substituted phenylhydrazones, o - semidenes, and a comparison of these with the results

Fig D 70ev

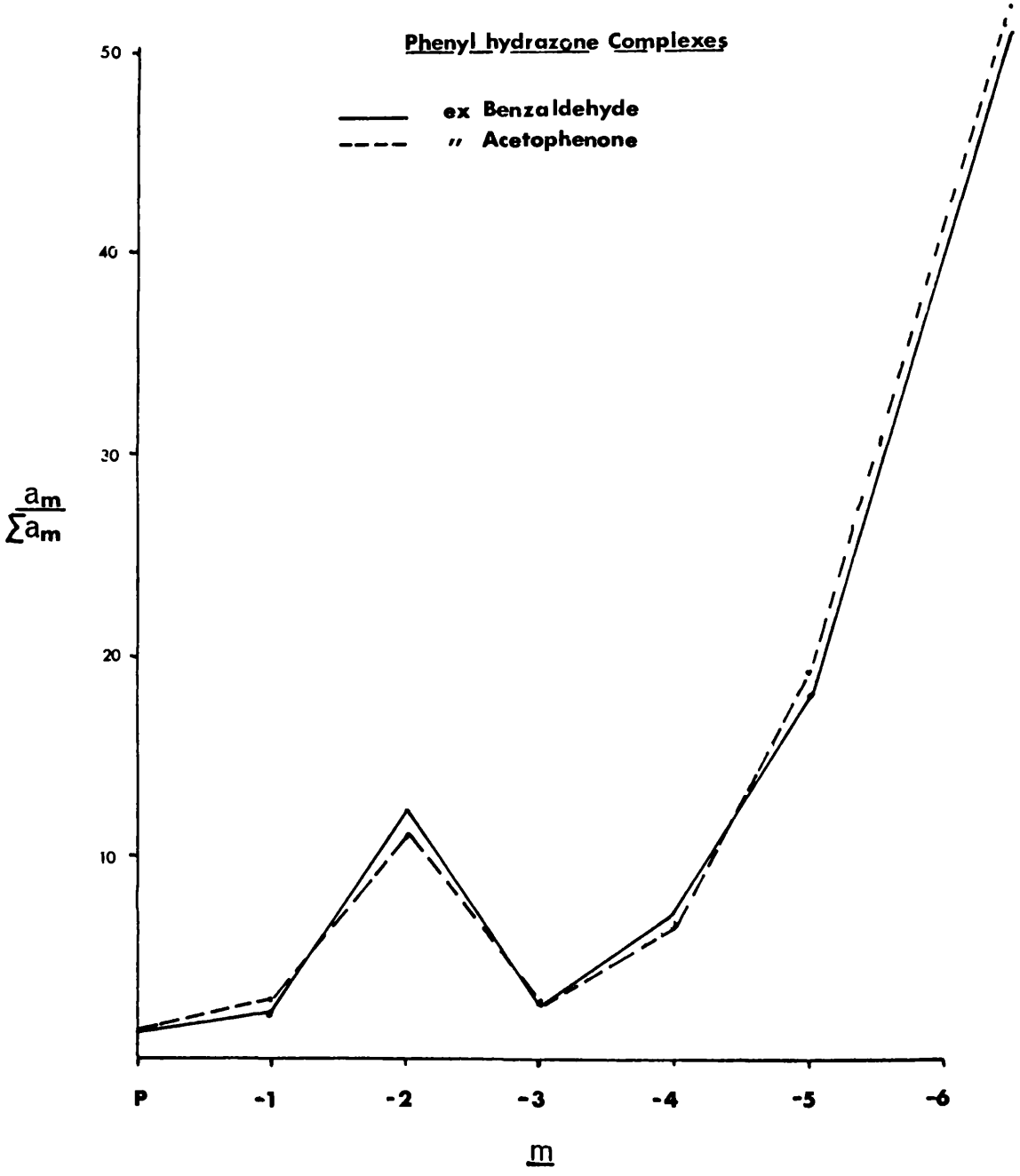

Phenyl hydrazone Complexes
ex Benzaldehyde
" Acetophenone
50
40
30
20
10
$\frac{a_m}{\sum a_m}$
P
-1
-2
-3
-4
-5
-6
m

Fig E 70ev

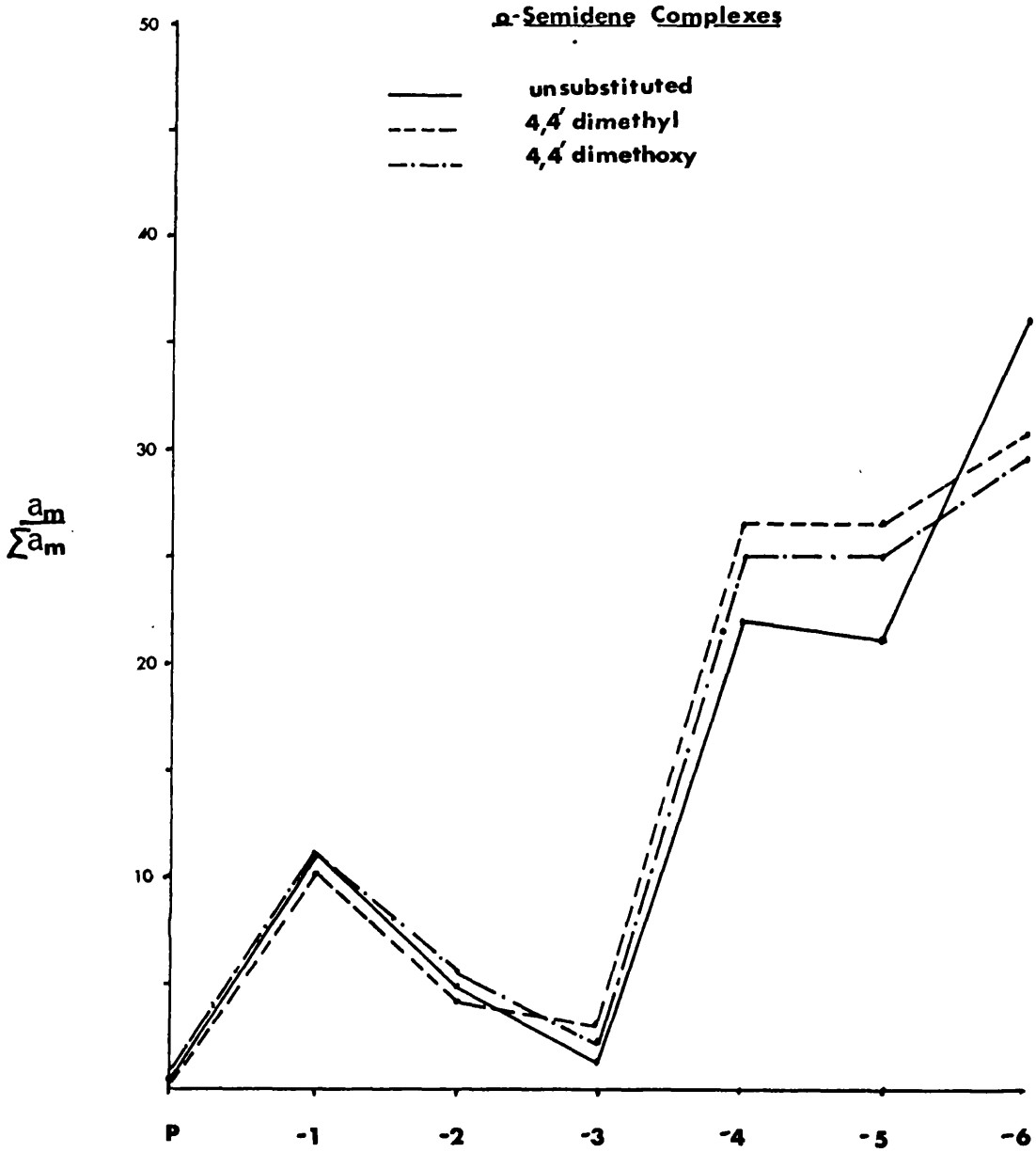
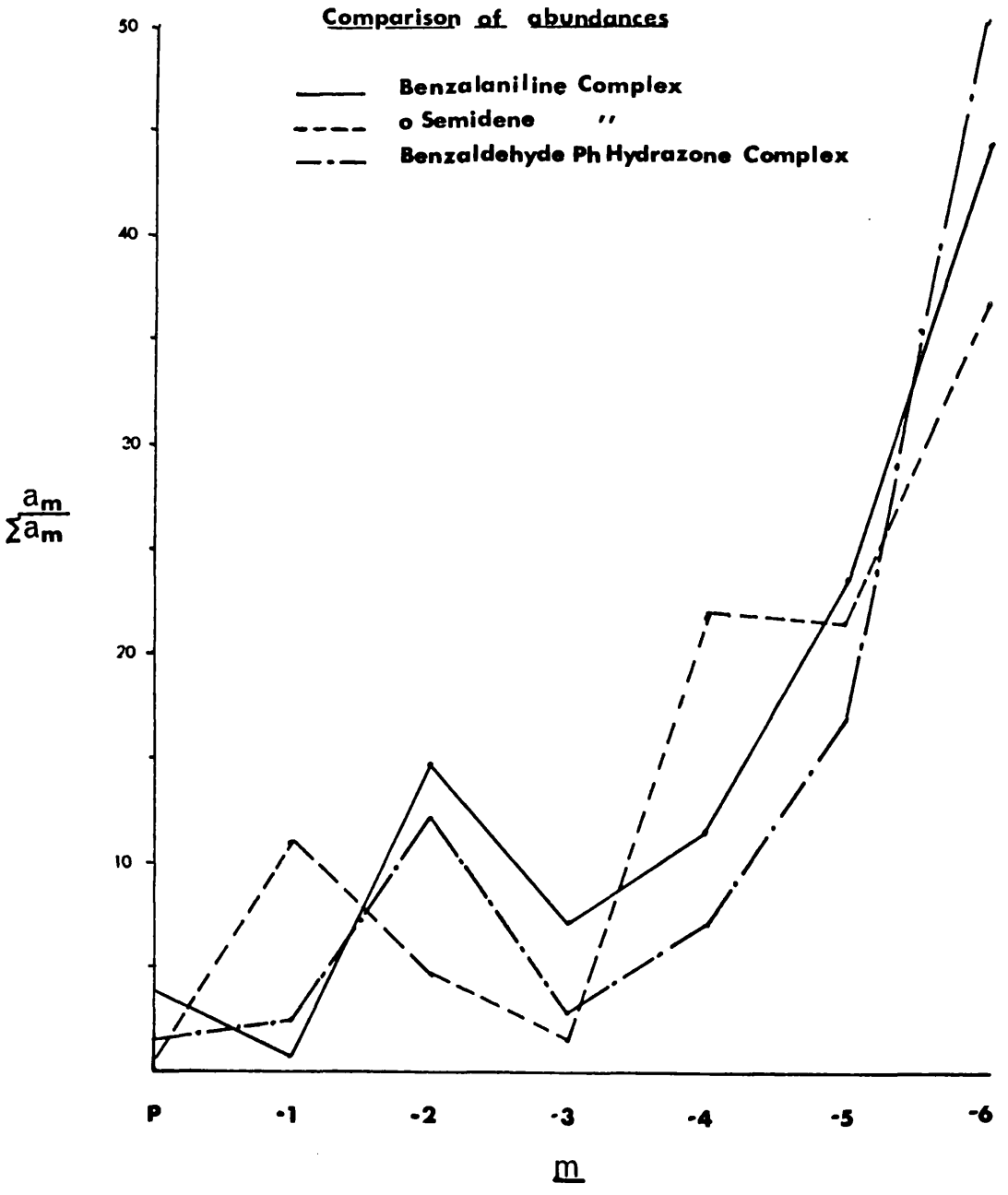

α-Semidene Complexes
unsubstituted
4,4′ dimethyl
4,4′ dimethoxy
50
40
30
20
10
$\frac{a_m}{\sum a_m}$
P
-1
-2
-3
-4
-5
-6

Fig F 70ev


Comparison of abundances
Benzalaniline Complex
o Semidene ''
Benzaldehyde Ph Hydrazone Complex
50
40
30
20
10
$\frac{a_m}{\sum a_m}$
P
-1
-2
-3
-4
-5
-6
m

from benzalaniline.

It is, therefore, possible to distinguish between complexes of these structural types with only the limited knowledge of the abundancies of the ions (m), a feature which has already proved useful in deciding that the compounds 7($R_1 = C_6F_4$, $R_2 = H$, $R_3 = C_6H_5$) and 8($R_1 = C_4H_2S$, $R_2 = H$, $R_3 = C_6H_5$) belonged to the benzalaniline structural type; although these were formed by particular rather than the usual reactions.

At this stage it is not possible to produce any further concrete evidence for the theories outlined but it is hoped that they will prove the basis for further experiments into the energetics of ionization and decomposition within these systems.

References (Appendix)

1. For a general review of these approaches see:-

   (a) F.A. Cotton and G. Wilkinson in, "Advanced Inorganic Chemistry", pp 560 - 609, John Wiley and Sons, New York, 1962.

   (b) F.A. Cotton in "Chemical Applications of Group Theory" p 183 - 244, Interscience, New York, 1965.

2. H. Bethe, Ann. Phys., 1929, 3, 133.

3. H.B. Gray and N.A. Beach, J. Amer.-Chem. Soc., 1963, 85, 2923.

4. A. Foffani, S. Pignataro, B. Cantone and F. Grasso, Z. Physik. Chem. (Frankfurt), 1965, 45, 79.

5. A. Foffani, S. Pignataro, G. Distefano and G. Inorta, J. Organometal. Chem. 1967, 7, 473.

† The A.E.I. MS9 mass spectrometer is equipped with an ion beam monitor which gives an indirect but not absolute measurement of the total ion current passing through the electrostatic analyser.

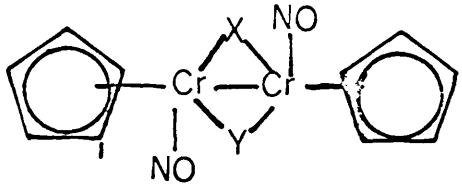
C H A P T E R 3

MASS SPECTRAL STUDIES IN BINUCLEAR METAL COMPLEX CHEMISTRY.

Introduction:

The discussion of the mass spectra of organometallic compounds in the literature (1) has been limited to the pthalocyanins, porphyrins, π cyclopentadienyl complexes, metal carbonyls, binuclear metal complexes and metal chelates. Without any doubt the factor which held up the application of mass spectrometry to this field was the notorious thermal instability of the compounds involved, but with the advent of direct insertion techniques (2) this difficulty has largely been overcome. Occasionally compounds are found which do not give parent ions but these are the exception rather than the rule, and it has been found during the course of this work that changing the insertion probe material often helps in stabilization of the compound. Probes are normally made of "pyrophilite" or alumina, the latter material being entirely unsuitable for experiments with organometalic carbonyl and nitrosyl compounds. It has been found, however, that the use of quartz probes improves the thermal stability of most iron chronium, manganese and nickel carbonyl complexes.

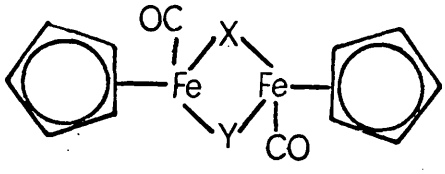
Thermal decomposition can also be minimized by correct choice of ion chamber temperatures as raising the temperature beyond an optimum volatilization level



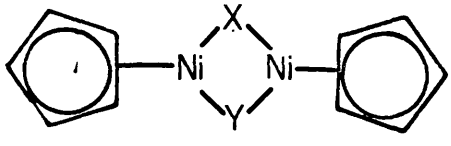
I X = Y = SMe IV X = Y = OMe

II X = Y = SPh V X = Y = OEt

III X = OH, Y = SMe VI X = Y = NMe_2



VII X = Y = SMe VIII X = Y = SPh



IX X = Y = SMe X X = Y = SEt

Fig 1

only decreases the abundance of the parent ion (3) due to an increase in the rate constants of its mass spectral decomposition reactions, but also increases the rate of thermal decomposition of the complex.

In the following section the mass spectral features of a number of cyclopentadienyl μ- mercaptido, μ-alkoxo, and μ- dialkylamido derivatives of chromium, iron and nickel (Fig. 1) will be discussed in terms of their cracking patterns and rearrangements. Mechanisms will be elucidated by means of labelling techniques.

Discussion

It is convenient to discuss the mass spectral characteristics of the compounds in terms of the metal atoms involved and variation of the bridging groups.

The mass spectra of several metal nitrosyl complexes with bridgedthiol systems have been reported very recently (4). These workers found the metal - sulphur ring structure to be the most stable grouping with primary loss of nitric oxide occurring in both the iron and cobalt series studied. Those complexes which contained μ- alkyl mercaptido groups, however, did not demonstrate complete removal of all nitrosyl groups before other fragmentations occurred, as is generally observed in metal carbonyl complexes (5). In the case

of bridging aromatic mercaptide groups, however, no competitive fragmentation of metal - nitrosyl and mercaptide bonds took place and, in general, they found that the decomposition pattern is more dependent on the nature of the side chain of the mercaptide unit than the metal atom.

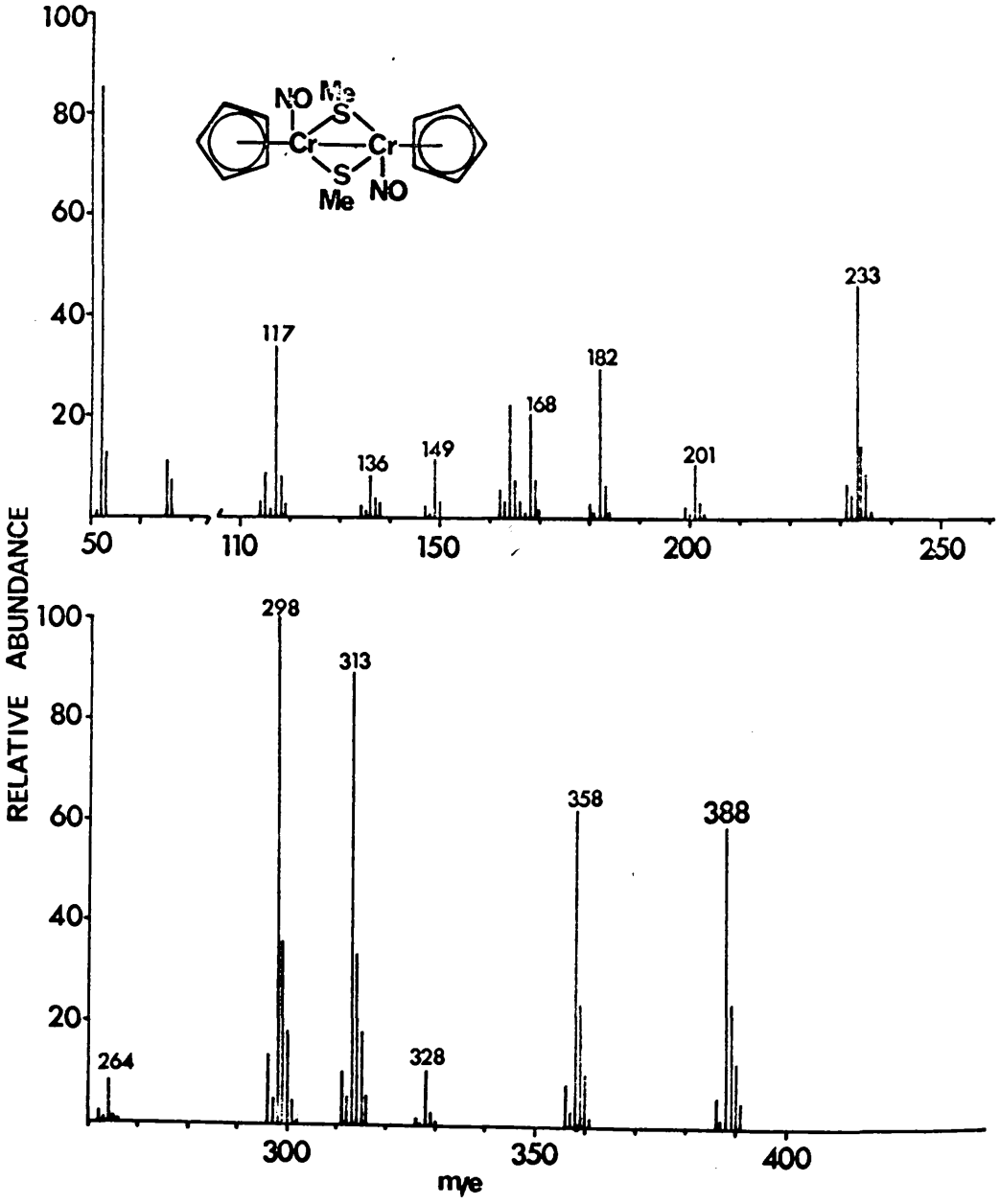
It is worthwhile to compare these results with those obtained from mercaptide bridged cyclopentadienyl chromium nitrosyls.

(a) Cyclopentadienyl μ - mercaptido, alkoxo and amido Complexes of Chromium

Although the nitric oxide group is a 3 electron donor believed to bond to the metal atom by first donating its odd electron, thus reducing the valency state of the metal by one unit (6) and allowing NO^+ to bond in a manner analogous to carbonyls, the concentration of charge density on the metal leads to the formation of a polar structure $M^{-1}-N^{+1}\equiv O$, but by analogy with the metal - carbonyl bond, stability is achieved by back acceptance of charge by the π^* antibonding NO orbitals from the filled hybrid orbitals of the metal. Other evidence also indicates better π accepting properties of nitrosyl groups as compared with carbonyls (7).

It has also been shown (8) that the σ - donor ability and π acceptor ability of ligands must be

Fig. 2


RELATIVE ABUNDANCE
100
80
60
40
20
NO
Me
S
Cr
Cr
S
Me
NO
117
136
149
168
182
201
233
50
110
150
200
250
298
313
264
328
358
388
300
350
400
m/e

considered together in evaluating their influence on properties like ionization potentials and vibration frequencies of complexes in which they participate. Generally speaking, in metal carbonyls and nitrosyls (9) increased back donation to the ligand system from metal causes a stiffening of the metal nitrosyl or carbonyl bond as is also the case in mixed nitrosyl - carbonyl systems (8). It was, therefore, expected that the nature of the μ-ligand in the chromium complexes studied should show some influence upon the relative stability of the metal - nitrosyl and metal - μ ligand bonds.

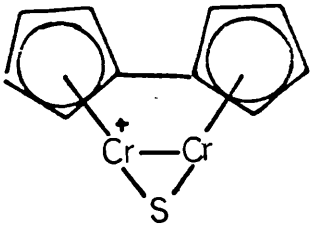
I. X = Y = SMe

In the mass spectral decomposition of this complex (Fig. 2) the first two steps involve stepwise loss of nitrosyl groups as had already been experienced in metal carbonyl systems. The P^+ and $(P - NO)^+$ at m/e 388 and m/e 358 respectively are of high abundance and hence reflecting the stability of the ligand system, although m/e 328 $(P - 2NO)^+$ ion is lower in abundance owing to the competing process of simultaneous elimination of nitrosyl and methyl groups from m/e 358 and supported by a metastable ion at m/e 300.5 (10).

It should be noted, however, that the doubly charged ion of the same molecular constitution as m/e 328, at m/e 164 is of high abundance (25%).

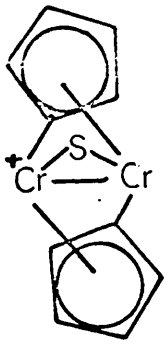
Unlike the bridged nitrosyl complexes discussed by Lewis (4), however, the base peak of the spectrum is at m/e 298 the $(P - 2NO - 2Me)^+$ ion, further fragmentation taking place from this ion by competitive losses of cyclopentadienyl and/or sulphur groups, thus evidence can be found in the spectrum for Cr^+, Cr_2^+, Cr_2S^+, $Cr_2S_2^+$, Cr_2Scyp^+, $Cr_2S_2cyp^+$, ions.

There are several ions of fairly high abundance, however, which do not fit into this simple ordered fragmentation scheme. These are notably the ions m/e 264, m/e 262 and m/e 182. Precise mass measurement of m/e 264 established its molecular formula as $C_{10}H_8Cr_2S$ and although no metastable is present in the spectrum for its formation it was suspected to have origins in elimination of hydrogen sulphide from m/e 298, the base peak of the spectrum. Such a process requires the migration of two hydrogen atoms to sulphur which must necessarily be from the cyclopentadienyl rings as no other source of hydrogen is available. In order to test this theory an isotopically labelled sample of the compound I was synthesised (X = Y = SCD_3) from the sodium



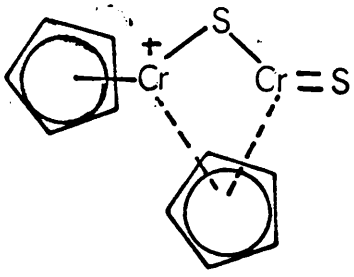
XI

or



XII

XIII



XIV

Fig 3

salt of trideuteromethyl mercaptan by the method of Ahmed and Knox (11). The labelled starting material used was trideutero methyl bromide (12), the mercaptan being made by an adaption of a previously published method (13).

The results of the mass spectrum proved the original postulate of H_2S elimination to be correct as the ion m/e 264 remained as such in the spectrum of the labelled complex and on the basis of this evidence two possible structures (XI and XII) are postulated for this ion (see Fig. 3).

M/e 232 was first suspected to be a rearrangement ion when closer examination of the ion abundancies revealed it to be some 4.2% greater in intensity than would be expected from isotopic contributions based on the intensities of the m/e 231 and m/e 233 ions. No change in the abundances of the ions m/e 231, 232 and 233 were recorded in the spectrum of the labelled complex and it was therefore concluded that m/e 232 was formed by elimination of a cyclopentadiene molecule from the most abundant ion m/e 298. The elimination of C_5H_6 from metal cyclopentadienyl systems is not unknown (14) and as the only hydrogens available for transfer are situated on the cyclopentadienyl

rings, a σ - π bonding system to the remaining cyclopentadienyl ring is postulated as in XIII (Fig. 3).

The third, and perhaps the most spectacular rearrangement, takes place in the formation of the ion m/e 182. Mass measurement gave its formula as $C_{10}H_{10}Cr$ which is attributed to the positively charged ion of chromocene, as further fragmentation supported by appropriate metastable transitions, occurs to yield ions at m/e 117, 65 and 52 (15). The formation of this ion was initially believed to be a thermal process, but a metastable ion at m/e 111.1 proves, in fact, that m/e 182 is formed by the electron impact dissociation of m/e 298 with elimination of CrS_2. Such a fragmentation involves the breaking of one chromium - chromium bond and two chromium - sulphur bonds together with the simultaneous transfer of a cyclopentadienyl ring. The driving force for this reaction is doubly favourable, as not only is the chromocene ion particularly stable but also elimination of a stable neutral is accomplished. It is proposed that an ion intermediate such as XIV occurs during the rearrangement process.

II. <u>X = Y = SPh</u>.

As in I the two primary processes of fragmentation from the parent ion m/e 512 involve

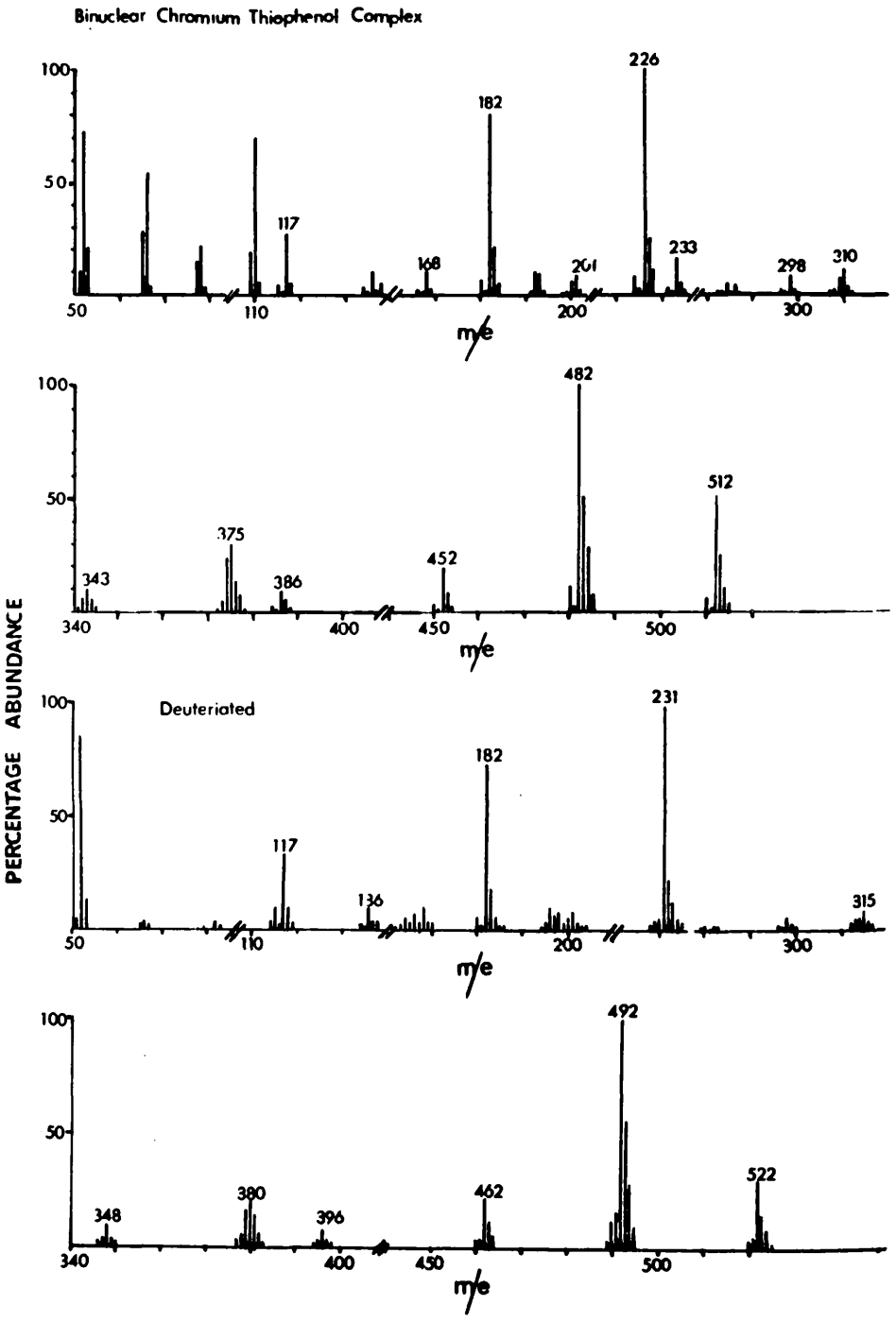
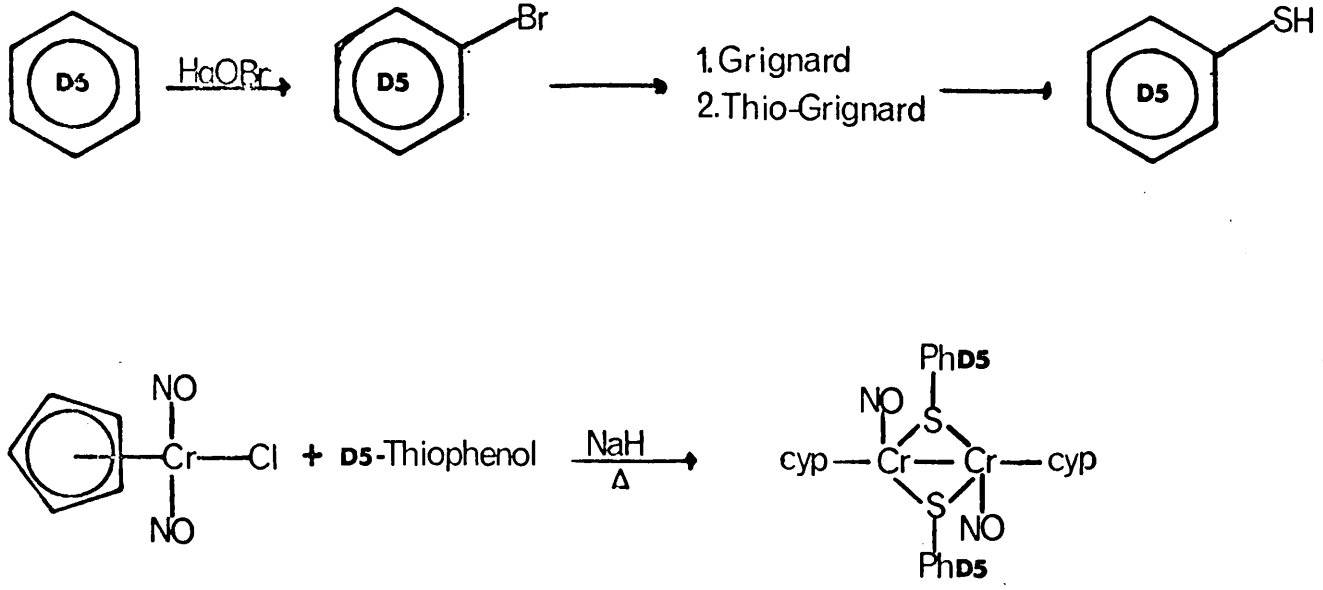

Binuclear Chromium Thiophenol Complex
PERCENTAGE ABUNDANCE
100
50
226
182
117
168
201
233
298
310
50
110
200
300
m/e
482
512
375
452
343
386
340
400
450
500
m/e
Deuteriated
231
182
117
136
315
50
110
200
300
m/e
492
522
380
462
348
396
340
400
450
500
m/e

Fig 4.

elimination of two nitric oxide molecules in stepwise fashion (Fig. 4). Unlike the case of methyl substitution, however, the base peak of the spectrum is m/e 482 the $(P - NO)^+$ ion. This is no doubt due to the participation of the phenyl groups in indirect bonding to the metal atoms through sulphur orbitals. The $(P - 2NO)^+$ ion is only of moderate abundance (20%) but is the origin of several modes of fragmentation, thus not only are the ions from simple fragmentations involving competitive loss of phenyl, cyclopentadienyl, or sulphur groups present in the spectrum but there is evidence that a large number of quite unusual rearrangement processes are taking place.

As in (I) ions corresponding to Cr^+, Cr_2^+, Cr_2S^+, $Cr_2S_2^+$, Cr_2Scyp^+, $Cr_2S_2cyp_2^+$ are to be found which can be easily accounted for by simple eliminations beginning from the $(P - 2NO)^+$ ion. The ions m/e 386, 374, 342, 201 and 182 and ions arising from them, however, must be formed by rearrangement and hydrogen transfer processes. M/e 386 considered to be formed by elimination of a cyclopentadiene molecule from the $(P - 2NO)^+$ ion, and supported by a metastable ion at 329.5* must involve hydrogen transfer from either of the two phenyl rings or the opposite cyclopentadienyl ring.

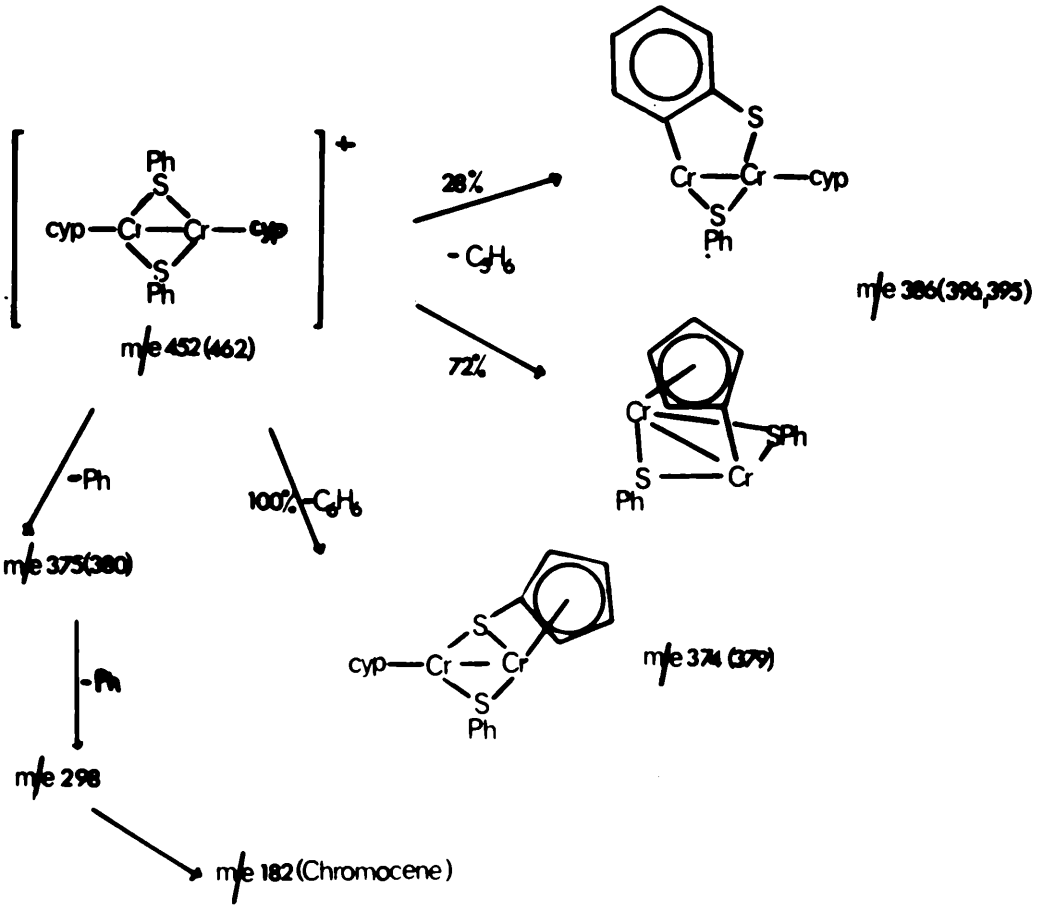
Fig. 5


D5
NaOBr
D5
Br
1. Grignard
2. Thio-Grignard
D5
SH
NO
Cr
Cl
NO
+ D5-Thiophenol
NaH
Δ
PhD5
NO
S
cyp
Cr
Cr
cyp
S
NO
PhD5

In order to facilitate the interpretation of the spectrum and to discover the sites of hydrogen transfer an isotopically labelled molecule of II with X = Y = SC_6D_5 was synthesised.. (D_5) Thiophenol was prepared from (D_5) bromobenzene (14) by an adaption of Tabury's method (17), and the labelled complex synthesised in the normal fashion (11). (See Fig. 5.)

A comparison of the spectra obtained for the labelled and unlabelled compounds is shown in Fig. 4. This method of labelling is particularly useful in that not only can the number of phenyl rings remaining in an ion species be seen at a glance, but also hydrogen transfers from the phenyl and cyclopentadienyl rings can be readily distinguished.

For instance, it can be easily seen that the ion m/e 386 in the spectrum of the unlabelled complex has now given rise to two ions m/e 396 and 395 in the spectrum of the labelled complex. This means that a cyclopentadiene molecule can be eliminated from the $(P - 2N_2)^+$ ion in two possible ways, either by hydrogen transfer from the other cyclopentadienyl ring, or from one or other of the two phenyl rings. Isotopic abundance measurements show that 72% of the hydrogen is transferred from cyclopentadienyl and 28% from phenyl.


Ph
S
cyp
Cr
Cr
cyp
S
Ph
+
m/e 452 (462)
28%
- C3H6
m/e 386 (396, 395)
72%
-Ph
100% - C6H6
m/e 375 (380)
-Ph
m/e 374 (379)
m/e 298
m/e 182 (Chromocene)

These figures, of course, do not take any account of possible isotope effects or of the fact that only the o - hydrogens on phenyl are sterically suited for transfer, thus giving a maximum of four possible origins of hydrogen, whereas all five positions on the cyclopentadienyl ring can be regarded as equivalent, and therefore must be regarded as a purely qualitative picture of the fragmentation process. The actual ion rearrangements themselves can be visualized as forming a Cr - benzene bond and a cyclopentadienyl - Cr bond respectively in the vacated sites. The structures proposed for the two forms of m/e 386 are shown in Fig. 6.

The ions m/e 375 and 374 of the unlabelled complex correspond to the elimination of a phenyl radical and a benzene molecule respectively from the $(P - 2NO)^+$ ion, the latter process necessitating hydrogen transfer to a phenyl ring during fragmentation. It can be readily observed from the spectrum of the labelled complex that the hydrogen migration occurs entirely from one or other of the cyclopentadienyl rings as the deuterium content is unaffected by benzene elimination and stabilisation of the ion occurring by

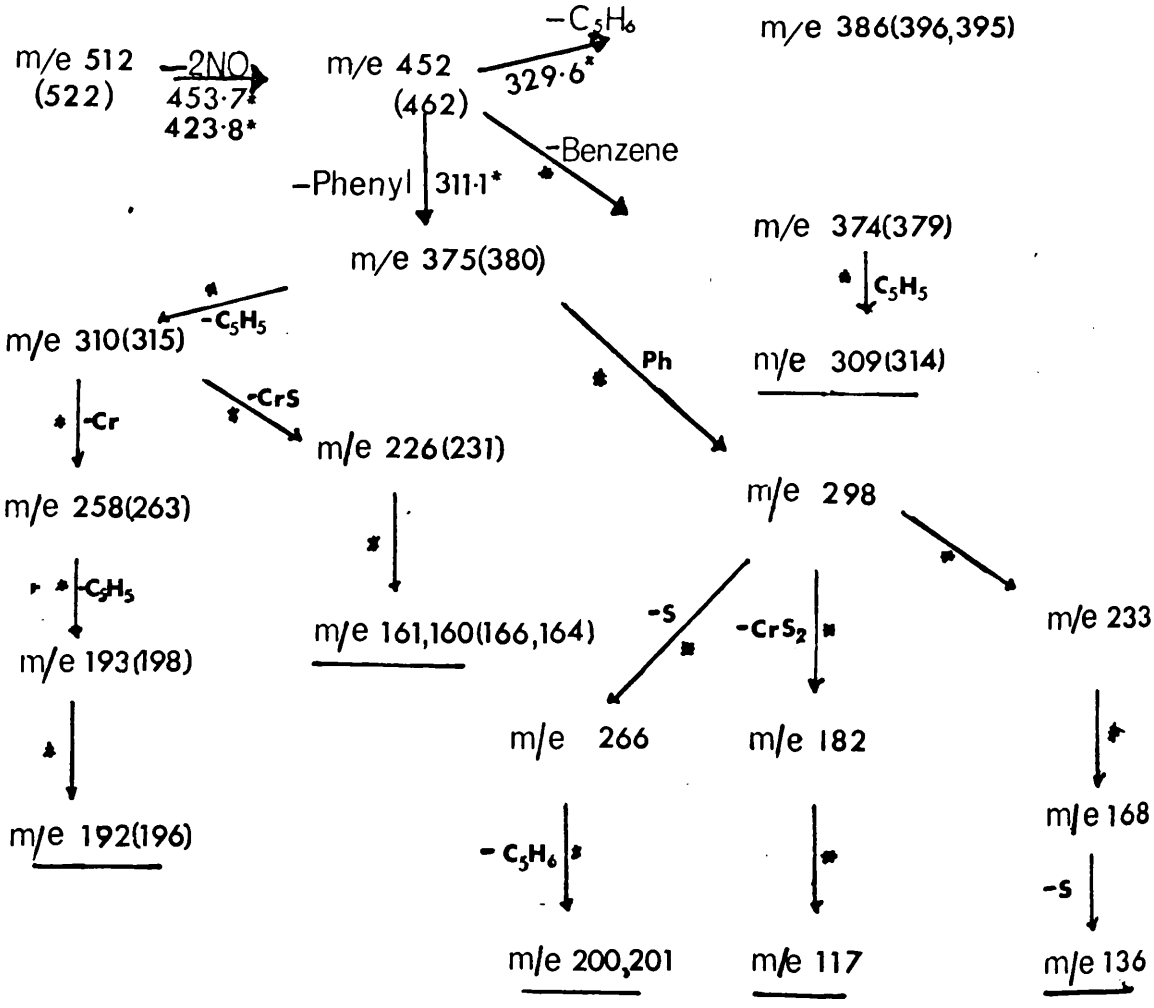

m/e 512 (522)
-2NO
453·7*
423·8*
m/e 452 (462)
-C5H6
329·6*
m/e 386(396,395)
-Benzene
-Phenyl
311·1*
m/e 375(380)
m/e 374(379)
-C5H5
-C5H5
m/e 310(315)
m/e 309(314)
Ph
-Cr
-CrS
m/e 226(231)
m/e 258(263)
m/e 298
-C5H5
m/e 161,160(166,164)
-S
-CrS2
m/e 233
m/e 193(198)
m/e 266
m/e 182
m/e 168
m/e 192(196)
-C5H6
-S
m/e 200,201
m/e 117
m/e 136

Fig 7

formation of a sulphur to cyclopentadiene bond as shown in Fig. 6.

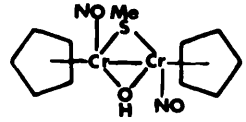
Similarly, the ions m/e 342 and m/e 233 are formed by elimination of SH from m/e 375 and m/e 266 respectively, the hydrogen originating entirely from a cyclopentadienyl ring accompanied by σ - bond formation to chromium.

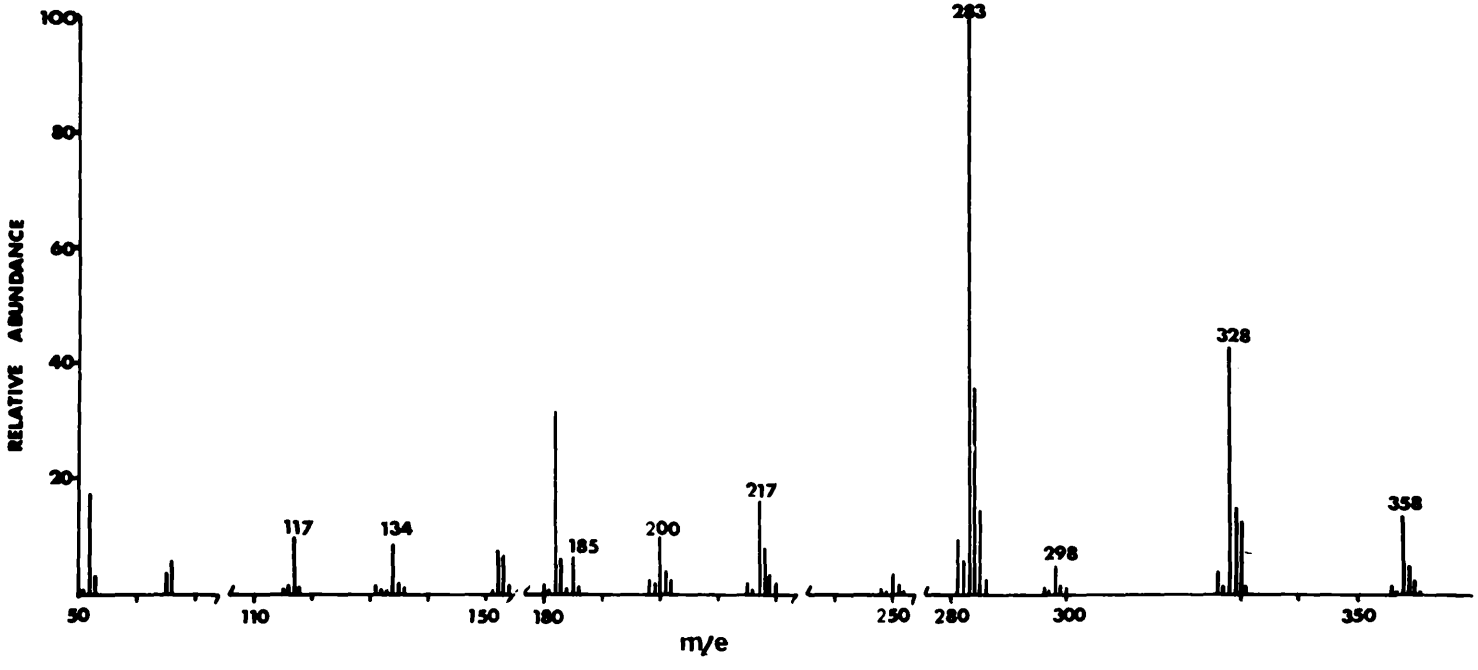
A complete flow diagram of the fragmentation processes of the complex can be seen in Fig. 7.

N.B. Ions in brackets represent the corresponding ions from the labelled complex.

III. X = OH, Y = SMe.

This compound was originally studied as an unknown formed in the same reaction as the methyl mercaptide complex (I). Mass measurement of the parent ion m/e 358 gave its formula as $C_{11}H_{14}OSN_2Cr_2$ and from the cracking pattern its structure was deduced to have an hydroxyl and an SMe bridge. This was further verified by equilibrating a solution of the complex in tetrahydrofuran with a potassium carbonate/D_2O solution. 96% exchange of the hydroxyl hydrogen took place, as shown by mass spectrometry, and not only did this verify the presence of an hydroxyl bridge, but also gave a great


NO
Me
S
Cr
Cr
O
H
NO

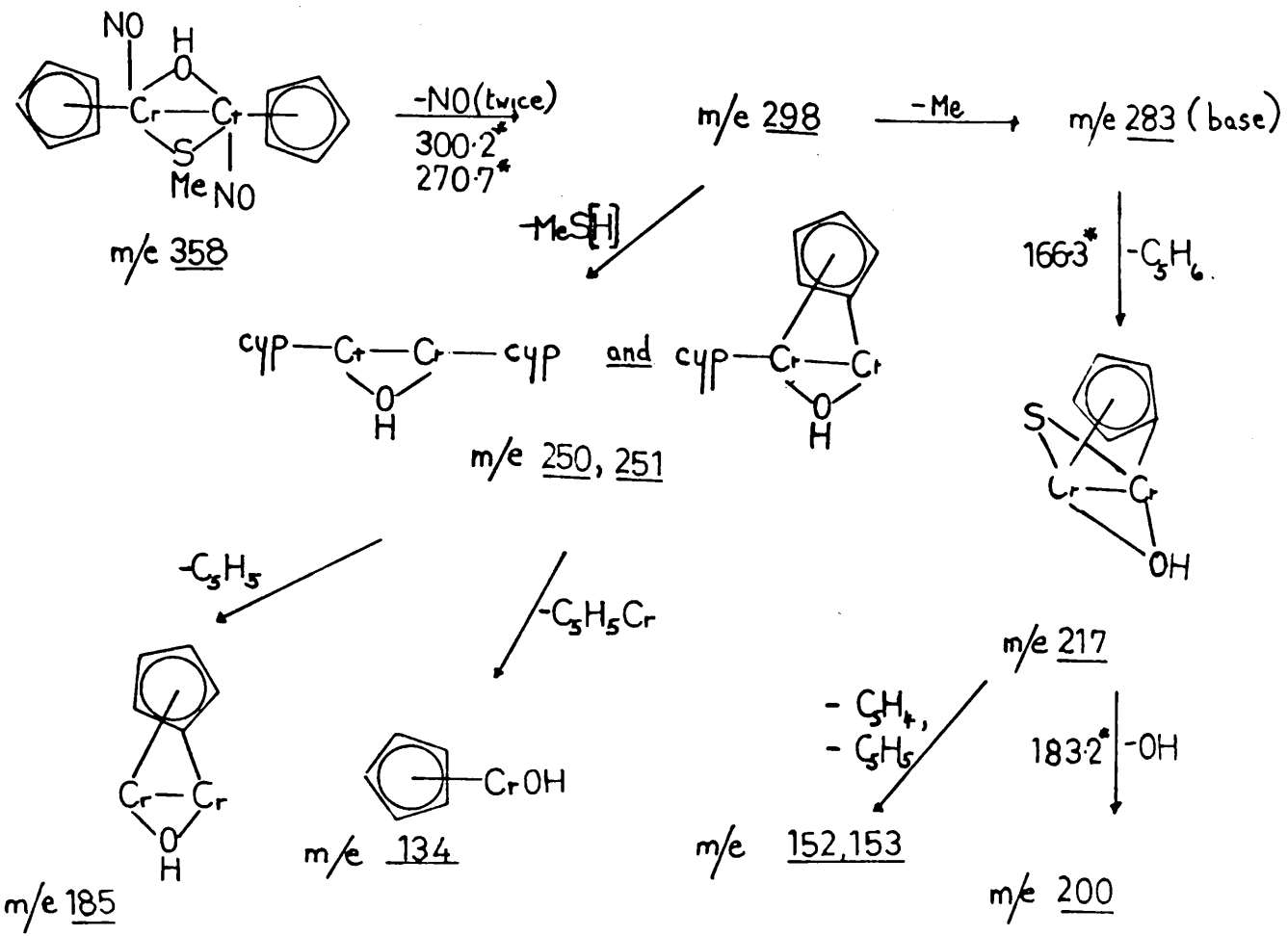

RELATIVE ABUNDANCE
100
80
60
40
20
283
328
358
217
117
134
185
200
298
50
110
150
180
250
280
300
350
m/e

deal of help in elucidating the structures of a number of rearrangement ions.

The parent ion of the complex which is of fairly high abundance (13%), as in all the bridged nitrosyls, gives two stepwise eliminations of nitric oxide to yield the ion m/e 298 (See Fig. 8). Fragmentation then takes place either by loss of a methyl radical to yield the base peak in the spectrum, m/e 283. It should be noted here in comparison that the base peak of the spectrum of (I) was the $(P - 2NO - 2Me)^+$ ion, a reflexion on the extra ion stability gained on fission of the sulphur - methyl bond.

After this point in the fragmentation process, all fissions involve the same kind of rearrangement process, and it is in this respect that deuterium proves really useful. For example, the formation of m/e 250, by elimination of methyl mercaptan from m/e 298 necessarily involves hydrogen transfer from a cyclopentadienyl ring as retention of deuterium occurs in the corresponding ion of the labelled complex.

Similarly the elimination of a cyclopentadiene molecule from m/e 283 involves participation of the other cyclopentadienyl ring in hydrogen transfer with


NO
H
O
Cr
Cr
S
Me
NO
m/e 358
-NO(twice)
300·2*
270·7*
m/e 298
-Me
m/e 283 (base)
-MeS[H]
166·3*
-C5H6
cyp
Cr
Cr
cyp
O
H
and
cyp
Cr
Cr
O
H
m/e 250, 251
S
Cr
Cr
OH
-C5H5
-C5H5Cr
m/e 217
- C5H4,
- C5H5
183·2*
-OH
Cr
Cr
O
H
m/e 185
Cr OH
m/e 134
m/e 152,153
m/e 200

the concomitant formation of a carbon - chromium σ - bond as has already been discussed in II and III. In fact it can be said that, apart from the formation of m/e 152 where deuterium was found to be transferred from the hydroxyl bridge to the multiply bonded cyclopentadienyl ring in its elimination, the tendency for the hydroxyl bridge to remain as such is very great.

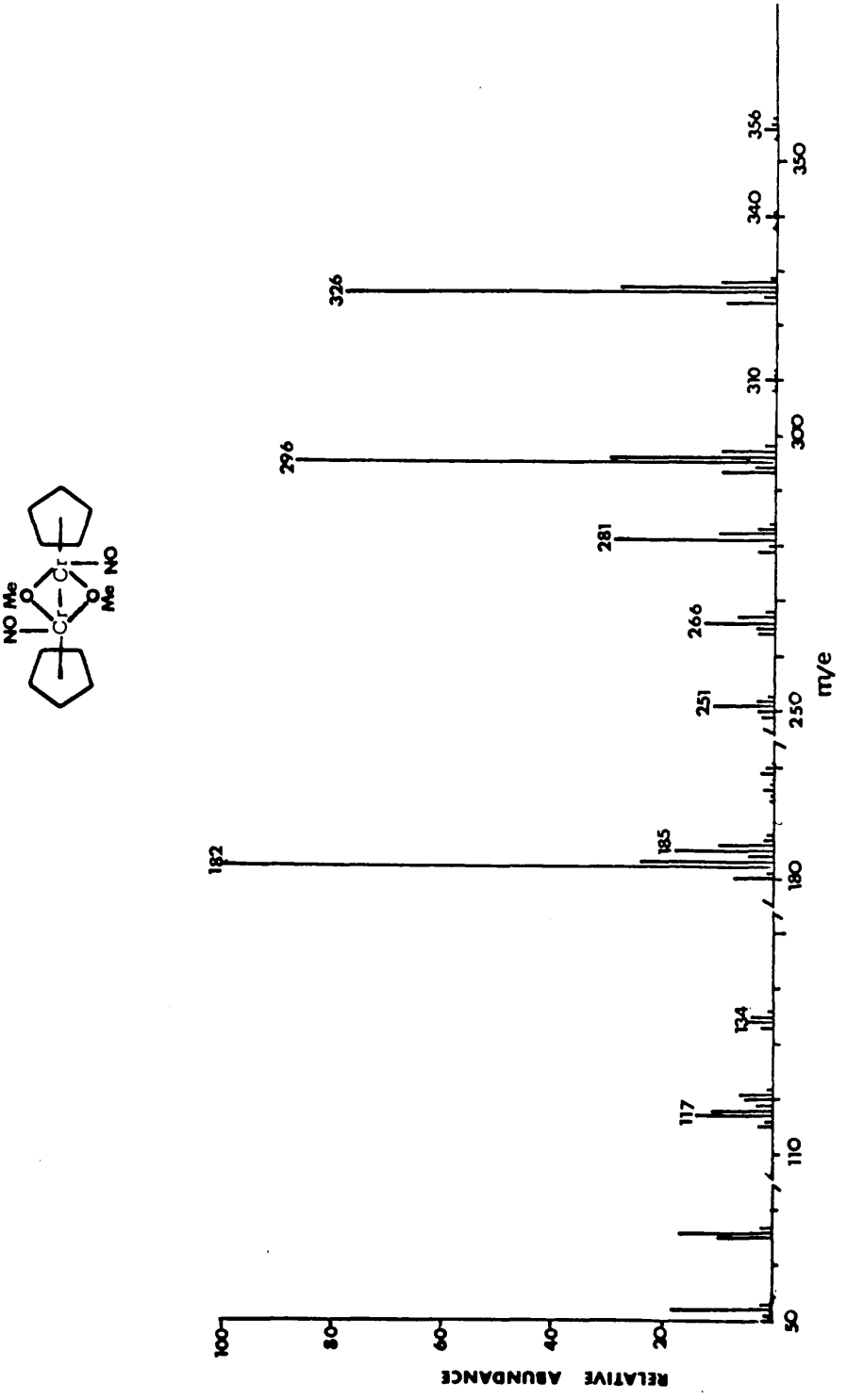
Last, but not least, it should be noted that the base peak of the spectrum m/e 283 eliminates a CrSOH fragment to form the exceptionally stable chromocene ion. This is consistent with the behaviour of I and II where the precursor of the rearrangement is the ion m/e 298 and the fragment eliminated CrS_2. A full diagramatic representation of the mass spectral decomposition is shown in Fig. 9.

IV and V. X = Y = OMe, X = Y = OEt).

It is useful to discuss the spectra of both these compounds under the same heading of oxygen bridging.

The immediate observation which one can make about the effect of oxygen bridging is on the stability of the molecular ion (Fig. 10). In both complexes the parent ion is of very low abundance ($<3\%$) which is no

Fig. 10


NO Me
Me NO
Cr
Cr
O
O
RELATIVE ABUNDANCE
100
80
60
40
20
m/e
50
110
180
250
300
350
340
310
356
326
296
281
266
251
185
182
134
117

doubt due to the weaker bond which must be formed between chromium and oxygen, because of the poor π - acceptor properties of the latter. This is also reflected in the chemistry of these compounds as the alkyloxo - bridges appear to be capable of easy displacement by mercaptide anion (18).

Elimination of one nitrosyl group, however, stabilizes the ion to a large extent due to the greater availability of metal orbitals for bonding to oxygen. A second elimination of nitrosyl results in a stable ion of even greater abundance (IV = 86%, V = 60%) and in this case reflects a stability greater than the $(P - 2NO)^+$ ion of II.

There exists, however, a mode of fragmentation from the P^+ and $(P - NO)^+$ ions in IV, however, which has no precedent in either I, II or III nor in the spectrum of published bridged nitrosyl complexes(4). This involves the elimination of 16 mass units in the formation of the ions m/e 340 and m/e 310. Precise mass measurement of these ions showed, in fact, that this corresponds to loss of a methane molecule in each case which can only arise by fission of the sulphur methyl bond together with transference of

Fig. 11

Chromocene+
cyp
Cr
R
O
P-2NO
-R
m/e 251
m/e 250
m/e 266
m/e 185
m/e 134
CrOH
H

hydrogen from one of the cyclopentadienyl rings, once more demonstrating the extraordinary driving force towards formation of a $\sigma - \pi$ bonded cyclopentadienyl system. It is difficult to find a reason why this should happen specifically in this molecule, but it may be that such an elimination tends to increase the stability of the oxygen bridge system by allowing better π acceptance through the cyclopentadienyl ring. This process, of course, does not occur from the $(P - 2NO)^+$ ion where a greater stability has been assumed.

The nature of fragmentation of both IV and V from the $(P - 2NO)^+$ ion is summarized in Fig. 11. The chromocene ion, which in the case of alkoxo bridging, is always the base peak of the spectrum, is formed directly from the $(P - 2NO)^+$ ion by elimination of a neutral $Cr(OR)_2$ fragment. This feature amply demonstrates the fact that substituted oxygen bridges tend to retain the alkyl group during the formation of chromocene. This is to be compared with the μ-mercaptido complexes I and II where alkyl and aryl substituents on sulphur were eliminated and the intermediate case of the mixed μ-hydroxo mercaptido bridged complex III where the methyl

substituent on sulphur was lost and the hydroxyl retained before chromocene formation.

Two other fragmentation routes are possible from the (P - 2NO)$^+$ ion. The first process involves hydrogen transfer to chromium from the alkoxo group during its elimination, and has precedent in neither I, II or III, nor in the spectra of other published bridged nitroso complexes (4). Elimination of the alkyl group from this ion thus produces m/e 251 an ion common to the spectra of both IV and V. By the reverse process m/e 251 can be formed by preliminary elimination of the alkyl group from the (P - 2NO)$^+$ ion followed by elimination and hydrogen rearrangement.

The ions m/e 134 and m/e 185, which are common to both spectra and which it should be remembered are decomposition products of III, are given the structures depicted in Fig. 11 on an analogy with their known constitution in the spectrum of III.

A table of precise mass measurements made on these compounds to distinguish the various different possible contitutions of the ions is shown in Table 1.

Table 1

m/e	Measured Mass	Formula
340	339.96038	$C_{11}H_{12}N_2O_4Cr_2$
326	325.99372	$C_{12}H_{16}NO_3Cr_2$
310	309.96248	$C_{11}H_{12}NO_3Cr_2$
296	295.99538	$C_{12}H_{16}O_2Cr_2$
266	265.98504	$C_{11}H_{14}OCr_2$
185	184.91480	$C_5H_5OCr_2$
134	133.99204	C_5H_6OCr

It is worthwhile to mention here that the elucidation of the decomposition pathway of IV made it possible to determine the structure of V. Compound V was obtained as an unknown compound from a reaction between cyclopentadienyl chromium dinitrosyl chloride and excess lithium diphenylamide, whilst attempting to introduce a diphenyl amide ligand on to chromium. The reaction, however, was performed in diethyl ether which no doubt reacted with the phenyl lithium present to produce ethoxyl radicals and hence the bridged complex V.

V. $\underline{X = Y = NMe_2}$.

Neither nitrogen nor oxygen possesses d orbitals for back donation from the metal atom but

Fig. 12

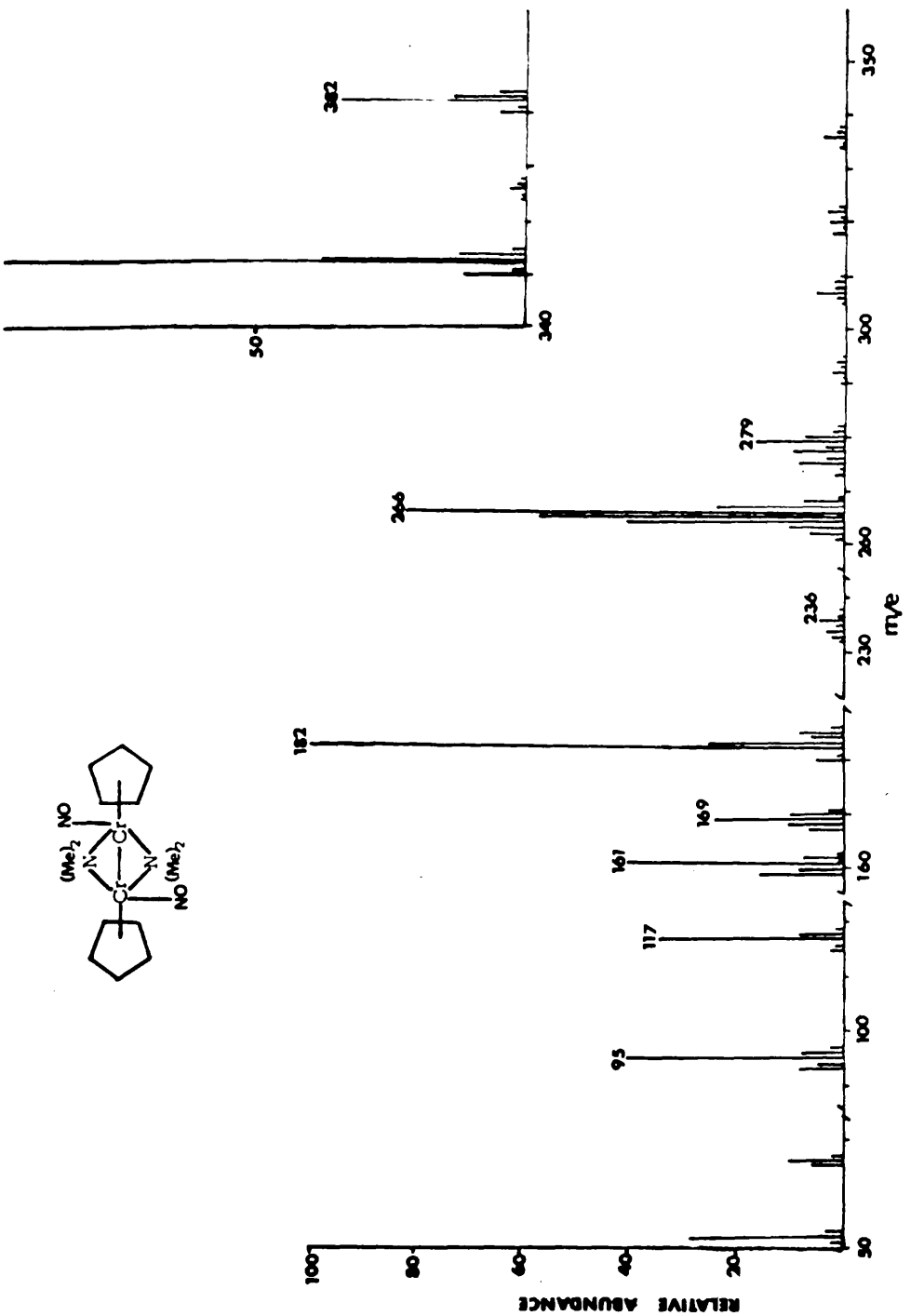
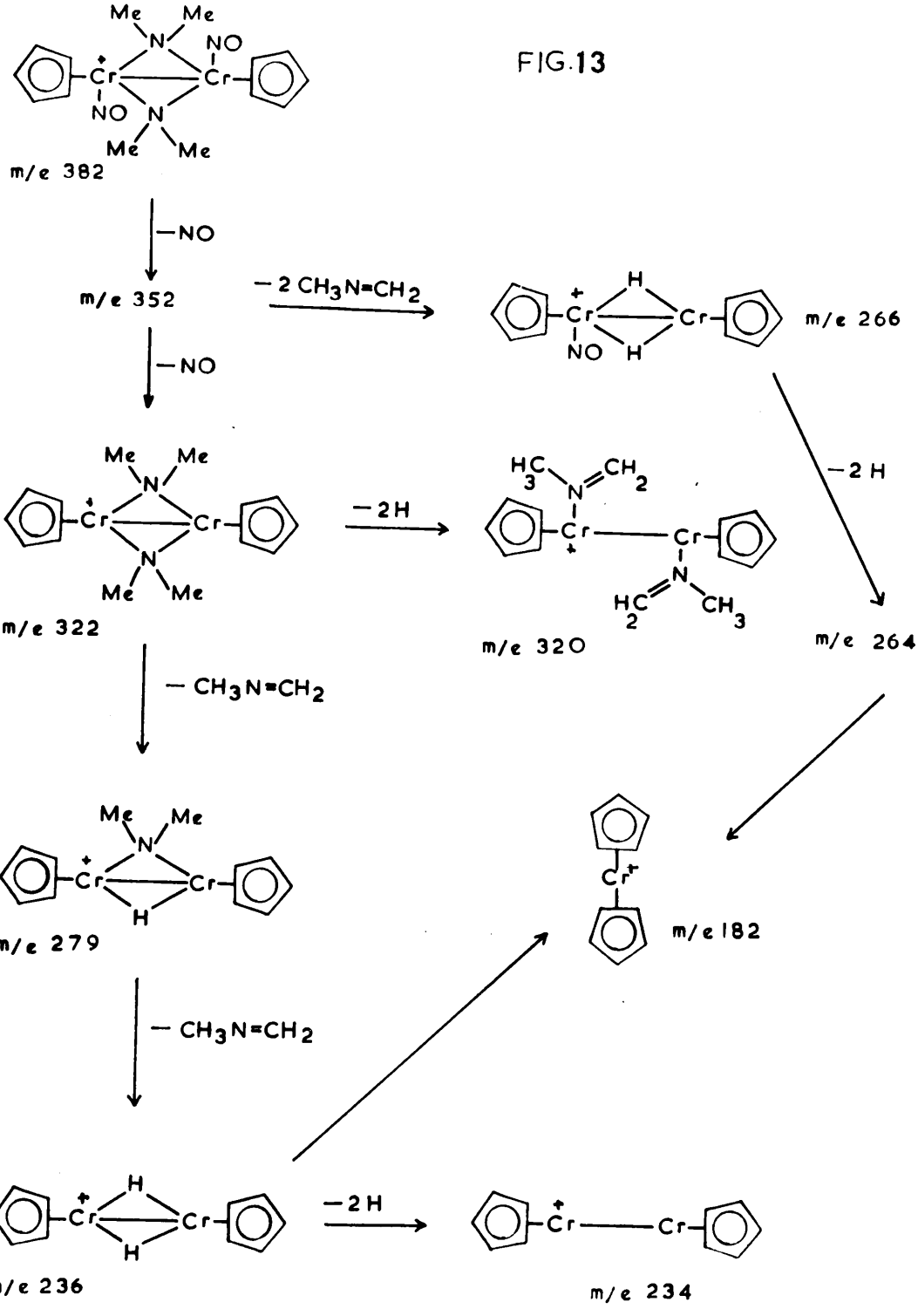

RELATIVE ABUNDANCE
100
80
60
40
20
50
m/e
100
150
200
250
300
350
182
246
279
95
117
161
169
236
340
382
NO
(Me)2
N
Cr
NO(Me)2

FIG. 13


m/e 382
−NO
m/e 352
−NO
−2 CH3N=CH2
m/e 266
m/e 322
−2H
m/e 320
−2 H
m/e 264
−CH3N=CH2
m/e 279
−CH3N=CH2
m/e 182
m/e 236
−2H
m/e 234

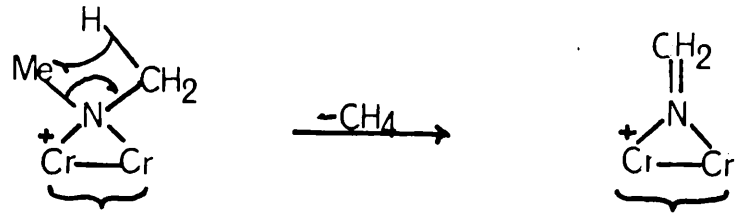
nitrogen is known to be a better donor, and in this sense, is intermediate in type between sulphur and oxygen. The effect of this on the nature of the mass spectral decomposition of VI is quite striking.

The major route of fragmentation stems, in fact, from the $(P - NO)^+$ ion (See Figs. 12 and 13) and not as has been the case previously from the $(P - 2NO)^+$ ion. In addition, the parent ion and the $(P - NO)^+$ both eliminate fragments of mass 16 which precise mass measurement has identified as methane.

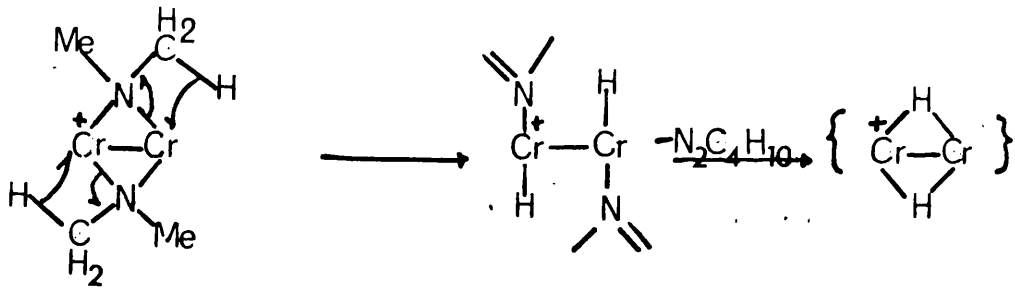
It will be recollected that IV also demonstrated hydrogen rearrangement and elimination of methane which was considered as formation of a bond between oxygen and the cyclopentadienyl rings. Although no labelling studies have been made on VI, however, it is more likely that the hydrogen transferred originates from the gem - dimethyl forming a four membered transition state as shown in Fig. 14A.

As has been noted in the mass spectra of other complexes with dimethyl amido ligands (19), there exists a driving force to eliminate 43 mass units, i.e. the dimethyl amido group minus one hydrogen as opposed to the entire ligand. This is undoubtedly due to the

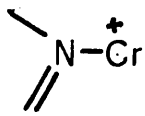
A



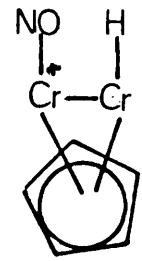
B



m/e 169



m/e 95



m/e 200

Fig 14

stabilization introduced by the "make and break" process of hydrogen transfer and ligand elimination, as well as the elimination of a stable imine.

Thus the $(P - 2NO)^+$ ion of VI demonstrates the successive elimination of two imine nuclei to form the ions m/e 279 and m/e 236, whilst the $(P - NO)^+$ ion shows the concomitant elimination of two imine groups as a mass loss of 86 in the formation of m/e 266, as shown in Fig. 14B. This double elimination, which has been noted previously in Chapter 2 p. 68 is supported by a metastable ion at m/e 201.0 and by the appropriate mass measurements.

Although the formation of the chromocene ion has been demonstrated to occur in all previously mentioned compounds of this group, in all cases evidence could be found only for one decomposition route for its formation. The mass spectrum of VI, however, is somewhat of an enigma in that there are three actual routes followed.

The first and main route occurs from m/e 266 by elimination of a fragment of constitution CrH_2NO and supported by a metastable ion at m/e 124.5, whilst the other two routes which are very similar to that observed in the previous complexes involve the

elimination of CrH_2 and Cr from m/e 236 and m/e 234 respectively.

Within the remainder of the spectrum several ions occur which do not have precedent: namely, m/e 200, m/e 169 and m/e 95 and for which the structures in Fig. 14 are proposed. The latter ion, which precise mass measurement has shown to be of formula C_2H_5NCr originates by disproportionation of $(P - 2NO - 2H)^+$ and in this respect is unparallelled in any known fragmentation for the bridged chromium complexes.

The origins of the other two ions are obscure, as no metastable ions can be found for their formation but it is likely that m/e 200 at least is formed directly or indirectly from m/e 266, by elimination of cypCr - H.

It should be noted that the spectra of both isomeric forms of this complex with cis and trans nitrosyl groups were examined and no observable difference could be found in either the nature of the cracking pattern or the intensities of individual ions. It is likely, however, that as primary fission occurs in a chromium nitrosyl bond, any steric differences present in the parent ion are lost and

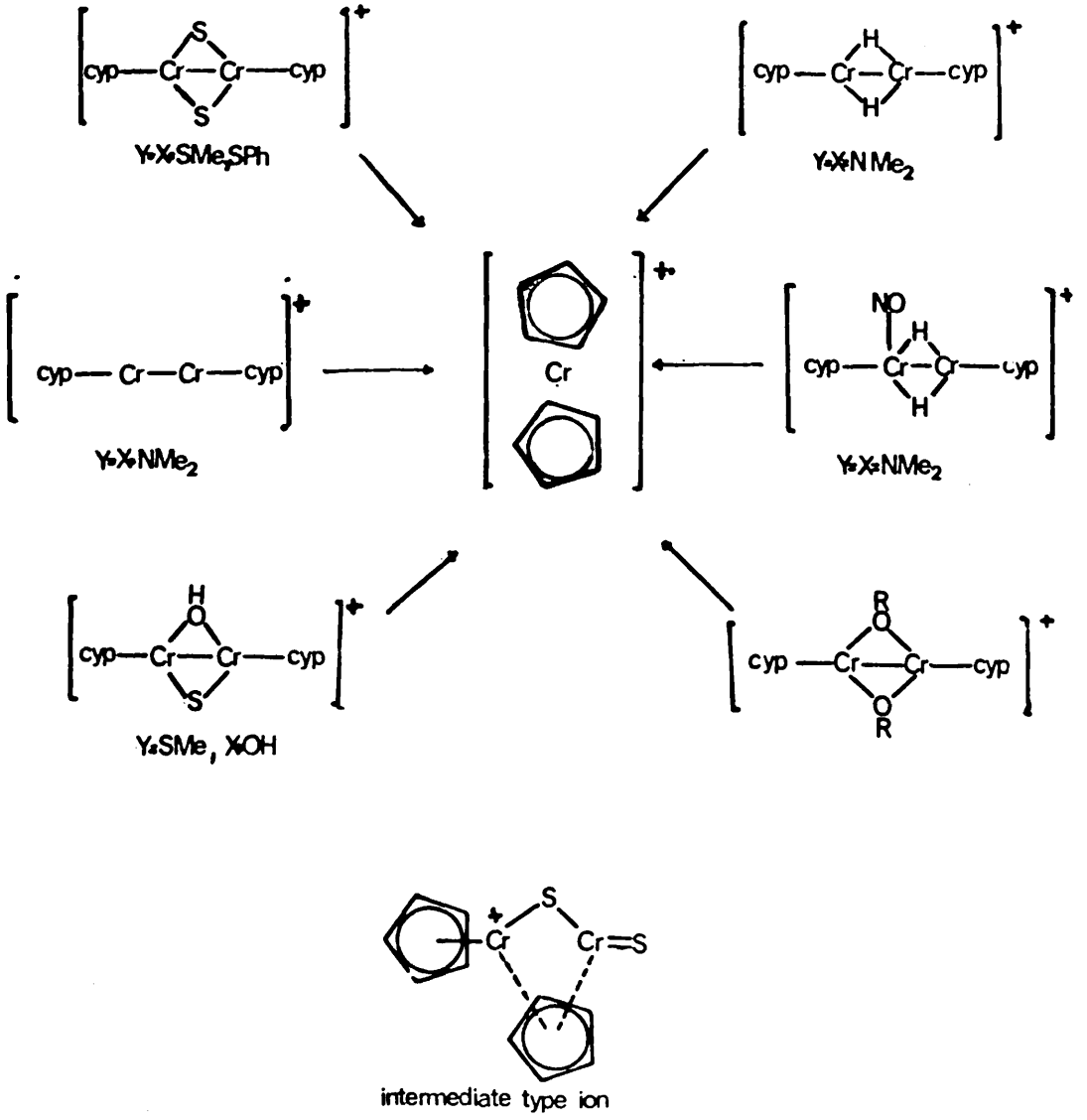
hence the $(P - NO)^+$ ion of both isomers can be considered as identical species.

Table 2

m/e	Experimental Mass	Formula
366	366.02354	$C_{13}H_{18}N_4O_2Cr_2$
336	336.02552	$C_{13}H_{18}N_3OCr_2$
279	279.01006	$C_{12}H_{17}NCr_2$
266	265.969633	$C_{10}H_{12}NOCr_2$
200	199.92563	$C_5H_6NOCr_2$
169	168.91989	$C_5H_5Cr_2$

In Conclusion

In can now be seen in the overall picture of fragmentation in the μ bridged chromium complexes studied that the effect of the bridging atom is particularly noticerble in the relative strengths of the ligand - metal and metal - nitrosyl bonds. Where a large amount of back donation can occur, as in the sulphur bridged complexes, fragmentation takes place preferentially in the metal nitrosyl bonds followed by fission of the sulphur - alkyl or aryl and/or metal cyclopentadienyl bonds. Lack


cyp—Cr—Cr—cyp
S
S
Y=X=SMe,SPh
H
H
Y=X=NMe2
Y=X=NMe2
NO
H
H
Y=X=NMe2
H
O
S
Y=SMe, X=OH
R
O
O
R
Cr
intermediate type ion

of back donation to the bridging heteroatom, however, produces a relative strengthening of the metal - nitrosyl bond; less apparent in oxygen which shows a small amount of competitive fission of the metal - nitrosyl and oxygen - alkyl bonds in addition to a ready secondary fission of the metal - oxygen bond, but readily observable in nitrogen where the ion current carried by fragments ions containing a nitrosyl group is greater than 7% of the total ionization current.

The effect of the bridging group is very noticeable also in decomposition to the chromocene ion. In both nitrogen and oxygen bridged structures, the m/e 182 ion is the base peak of the spectrum, whilst in the methyl mercaptide bridge it amounts to only 35% the abundance of the largest ion and the mixed μ alkoxo mercaptido complex being intermediate with an ion of 40%. A collective diagram of the routes of formation is shown in Fig. 15.

(b) Cyclopentadienyl mercaptide complexes of iron.

The compounds to be discussed in this section, namely VII and VIII, are isoelectronic with the corresponding bridged nitrosyl chromium complexes but differ in the fact that there is no metal - metal bond.

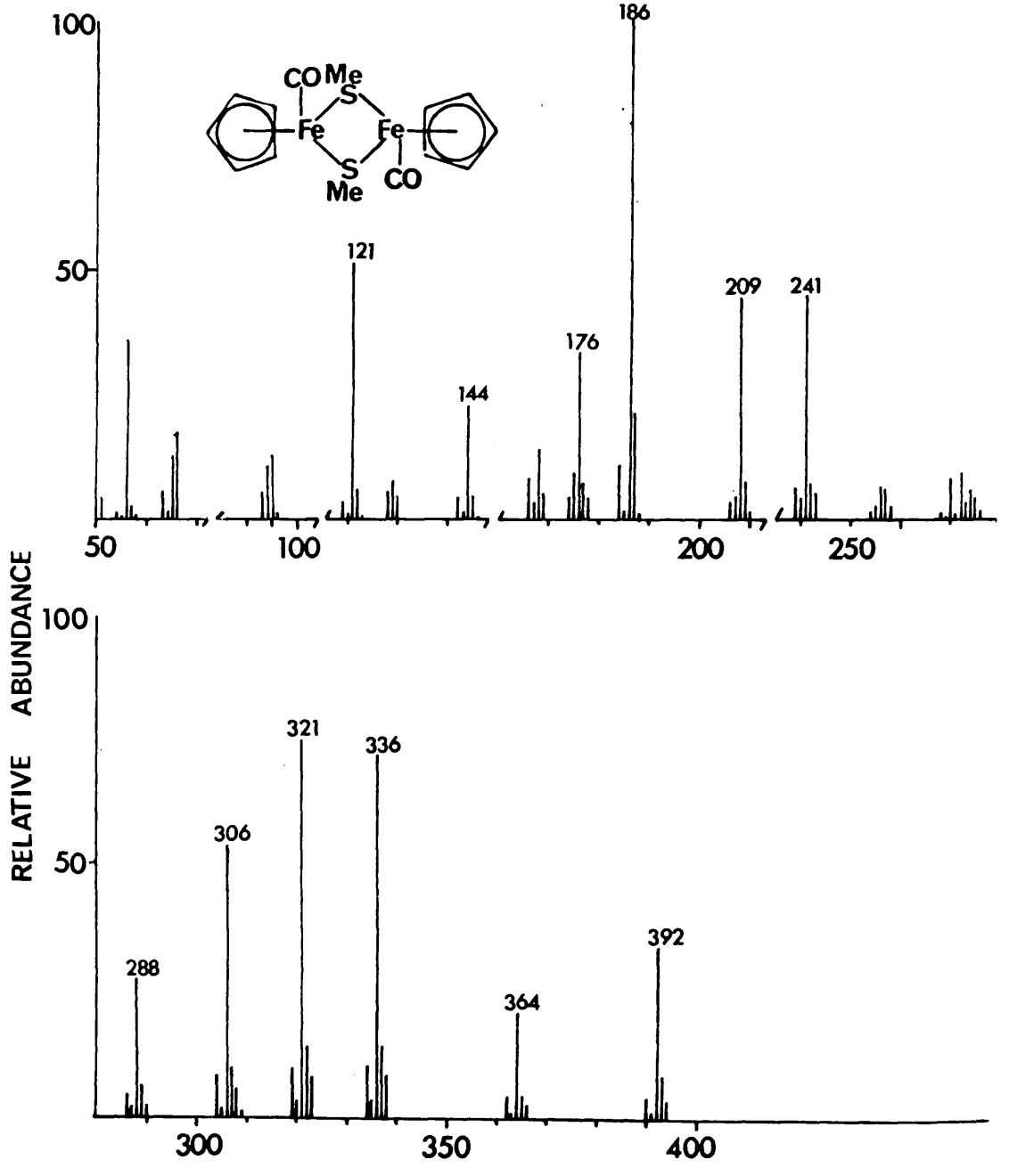
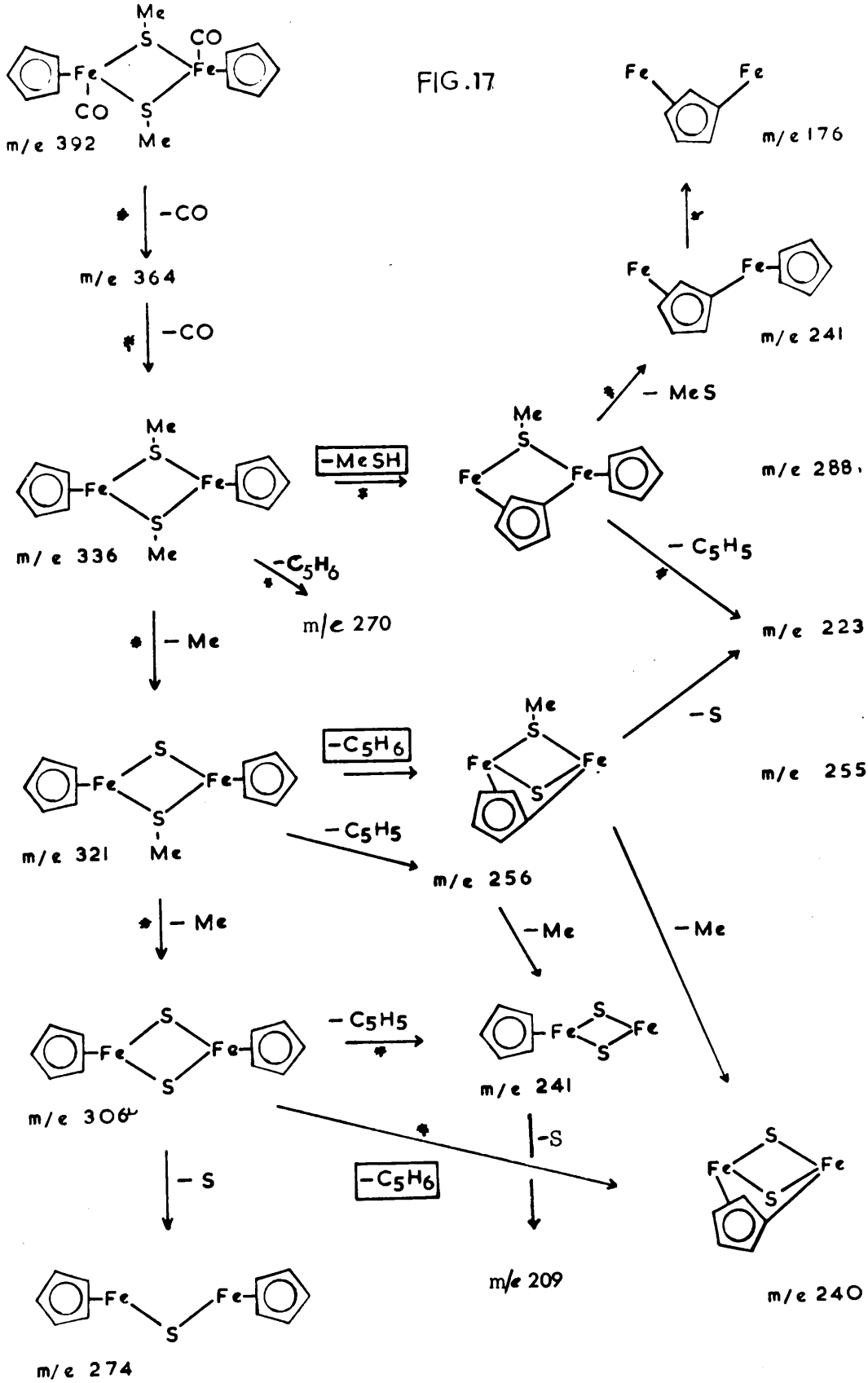

100
50
CO
Me
S
Fe
Fe
S
Me
CO
186
121
209
241
176
144
50
100
200
250
RELATIVE ABUNDANCE
100
50
321
336
306
288
392
364
300
350
400

FIG.17


m/e 392
-CO
m/e 364
-CO
m/e 336
-MeSH
m/e 288
-MeS
m/e 241
m/e 176
-C5H6
m/e 270
-C5H5
m/e 223
-Me
m/e 321
-C5H6
m/e 255
-S
-C5H5
m/e 256
-Me
-Me
-Me
m/e 306
-C5H5
m/e 241
-S
-S
-C5H6
m/e 209
m/e 240
m/e 274

VII. X = Y = SMe. (Fig. 16)

At first sight the mechanisms of fragmentation of VII appear to be very similar to those of I. Not only do primary fragmentations occur by fission of the metal carbonyl bonds, but also simple eliminations of methyl and cyclopentadienyl groups occur as in I. However, on closer examination, several additional routes appear possible and mass measurements have shown that several ions have constitutions at variance with what might be proposed on this simple fragmentation mechanism (Fig. 17).

For example, m/e 288 is formed by elimination of MeSH from the $(P - 2CO)^+$ ion and is supported by a metastable transition at m/e 246.8. Such an elimination necessarily involves hydrogen transfer from a cyclopentadienyl ring to form a $\sigma - \pi$ bonded system to iron, which has many precedents in the spectra of the bridged chromium complexes and which is further supported by elimination of MeS and a cyclopentadienyl ring to give the ions m/e 241 and m/e 176. The latter ion, it may be noted, was originally thought to be Fe_2S_2, but a precise mass measurement and observation of a metastable

ion at m/e 128.5* for its formation from m/e 241 established its identity and position in the above fragmentation (Fig. 17).

Additionally, elimination of a cyclopentadiene molecule occurs from the ions m/e 336, 321 and 306, the hydrogen transfer process being assumed to occur by the same mechanism as has been postulated in the chromium bridged complexes. It may be said here that all attempts to prepare the complex VII from CD_3SH by a similar method to that used in the preparation of the labelled complex of I failed to give the correct product and therefore verification of the mechanisms could not be made. The reason that this elimination is much more facile and occurs in a greater number of ions than in the corresponding chromium complex could be due to the absence of a metal - metal bond, and hence greater flexibility of the ring system.

Finally, the base peak of the spectrum m/e 186, which is attributed to the positively charged ion of ferrocene as it decomposes further to m/e 121 by elimination of a cyclopentadienyl radical (15), is thought to be of thermal origin as no metastable ions can be found for its formation. This is consistent with the known chemistry of bridged iron carbonyl compounds and their use

in the preparation of ferrocenes (20).

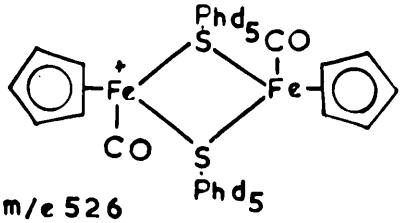
VIII. X = Y = SPh.

The thermal stability of this compound in the mass spectrometer is very small and it was found that a suitable spectrum could only be obtained when a quartz insertion probe was used. Even so, there are a large number of ions which can have thermal origin only. These are notably m/e 218 diphenyl disulphide and its related fragments m/e 141 and m/e 109; m/e 129 $C_5H_5S_2$; m/e 174 $C_{11}H_{10}S$; and m/e 186 the ferrocene ion.

It was noted, however, that electron impact dissociation did occur in such a way as to make it necessary that some labelling experiments be carried out. Thus the complex VIII with X = Y = SC_6D_5 was synthesised by a method similar to that of the labelled complex of II.

The results of this labelling experiment are very interesting in that the $(P - 2CO)^+$ ion, which originates by stepwise elimination of carbon monoxide from the parent ion, fragments with loss of cyclopentadiene to give an ion which has shown no deuterium transfer to the neutral fragment. Thus, unlike the corresponding chromium complex II, all the

FIG.18



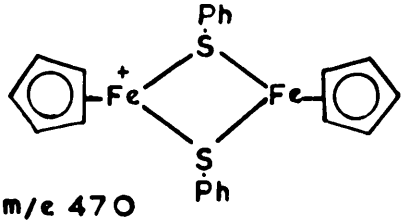
m/e 526

-CO

m/e 498

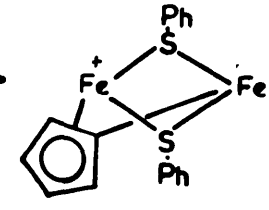
-CO

H transfer
100% from C_5H_5



m/e 470

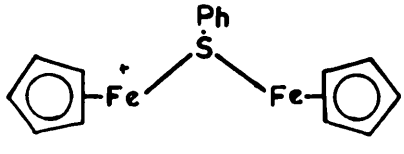
$-C_5H_6$



m/e 290

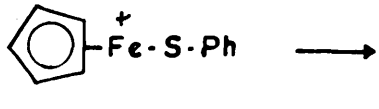
-PhS

m/e 404



No metastable ions corresponding to formation of $C_{18}H_{18}Fe$

m/e 356



m/e 121

m/e 235

hydrogen transferred originates from a cyclopentadienyl ring.

It can also be seen from Fig. 18 that no fragmentation of the sulphur phenyl bond occurs at any time and that C_6H_5S fragments are preferentially eliminated. It is also worthwhile mentioning that the stability of the $Fe_2S_2^+$ is not a driving force in the fragmentation process, and that the greater number of ions contain metal cyclopentadienyl bonds. In this respect, both VII and VIII are to be compared with the corresponding complexes in the chromium series already discussed.

(a) Cyclopentadienyl μ mercaptide Complexes of Nickel.

Unlike the complexes of chromium and iron already discussed, the mass spectra of IX and X are not of special interest.

It is worthwhile, however, to compare both complexes with their isoelectronic analogues in the chromium and iron series studied.

Preliminary fragmentation in both IX and X takes place by fission of the sulphur - alkyl bond and successive elimination of two methyl or ethyl groups are observed in the appropriate complexes. X, however, in a similar manner to the μ ethyl mercaptido complexes studied

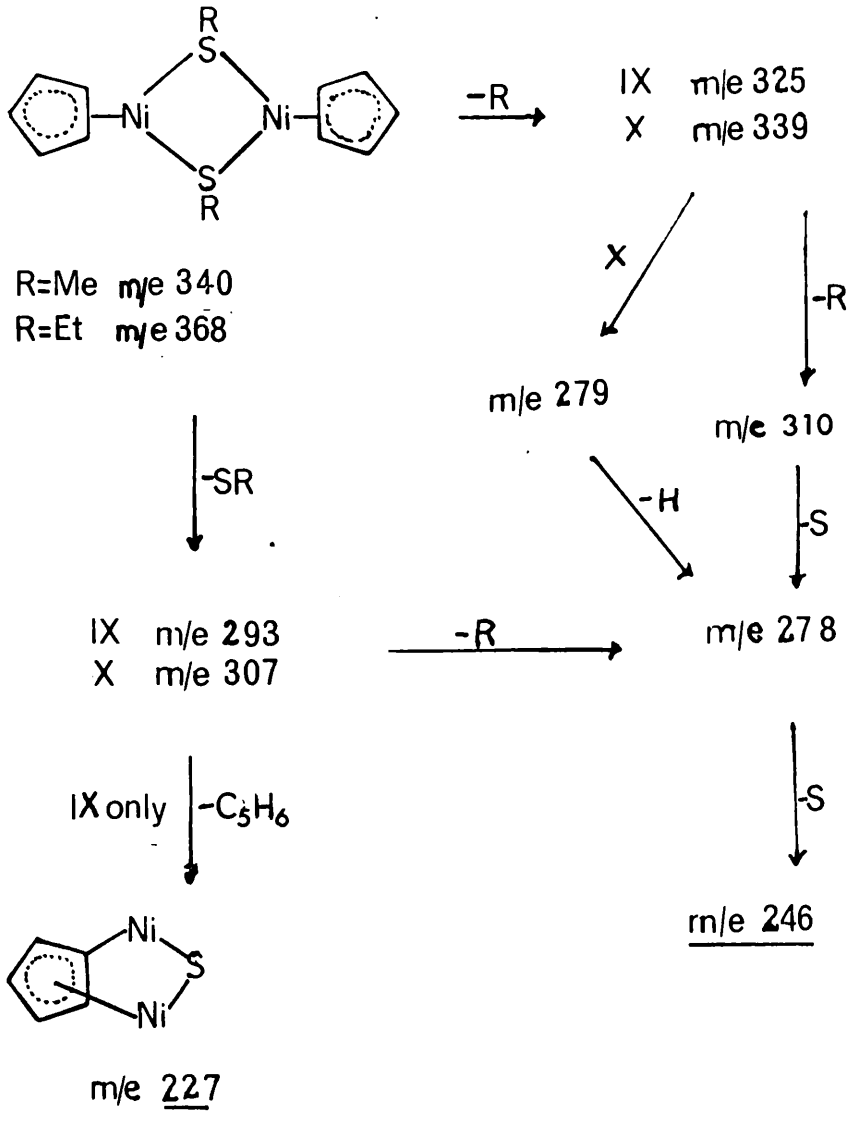

R
S
Ni
Ni
S
R
-R
IX m/e 325
X m/e 339
X
-R
R=Me m/e 340
R=Et m/e 368
m/e 279
m/e 310
-SR
-H
-S
IX m/e 293
X m/e 307
-R
m/e 278
IX only
-C5H6
-S
Ni
S
Ni
m/e 227
m/e 246

Fig 19

by Lewis (4) shows elimination with transfer of hydrogen to the metal atom except that in this case the sulphur atom is eliminated also, i.e. loss of $(CH_2)_2S$ from the $(P - Me)^+$ ion.

Also unlike the chromium - sulphur ring system of complexes I and II the nickel - sulphur ring system is unstable, and the driving force seems to be towards the formation of the ion m/e 246 Cyp_2Ni_2

Finally, only in a single fragmentation process is elimination of a C_5H_6 unit observed, that being from the $(P - MeS)^+$ ion of IX to form the ion m/e 227.

A summary of the fragmentation processes observed from IX and X is shown in Fig. 19.

Experimental

All mass spectra were run at a resolution of approximately 1000, on an A.E.I. M.S.9 mass spectrometer, at a source temperature of 150°C and using a direct insertion probe technique. Precise mass measurements were performed at a resolution of 10,000.

Reactions were carried out in an atmosphere of "oxygen free" nitrogen, further purified and dried by passing through Fieser's solution and concentrated sulphuric acid.

All reactions were performed in dried solvents and the products chromatographed on neutral alumina.

Preparation of D_5Bromobenzene (16)

A solution of mercuric oxybromide in 500 ml. water, prepared from bromine (53g., 0.66 mole) and mercuric oxide (160g., 0.55 mole) by the method of Houben (21) was shaken for 16 hours with D_6 benzene (8g., 0.09 mole). The lower layer was separated and dissolved in ether, and the resulting solution shaken with sodium carbonate solution to remove mercuric oxybromide. The solution was dried and distilled under vacuum to give D_5 Bromobenzene (10.39g., 60%). Isotopic Purity as determined by low voltage mass spectrometry 93% D_5.

Preparation of D_5 Thiophenol

Magnesium (1.8g., 0.04 mole) and a crystal of iodine were heated in a 500 ml. flask fitted with a condenser, dropping funnel and a gas inlet. The flask was then cooled, flushed out with dry nitrogen and 15 ml. sodium dried ether and D_5 bromobenzene (10.2g., 0.06 mole) added. When the reaction was initiated an additional 40 ml. ether was added and the flask cooled in an ice bath to avoid too vigorous reaction. When the reaction had subsided, the solution was gently refluxed for a further 30 minutes until the

magnesium had been totally dispersed and the solution assumed a dark brown colouration. The solution was then filtered into an ice cooled flask fitted with a condenser and pulverised sulphur (1.7g., 0.05 moles) added in small portions. The reaction was completed by gently refluxing for 30 minutes and the cooled solution hydrolysed by a mixture of 100 ml. 5% sulphuric acid and 25g. ice.

The ether solution was then dried and distillation gave D_5 Thiophenol b.p. 168° (3.5g., 50%). Isotopic purity as determined by low voltage mass spectrometry 91% D_5.

Preparation of Di - μ - (D_5)phenylthio - bis (cyclopentadienylnitrosyl chromium).

D_5 Thiophenol (1.1 ml. 0.01 mole) in tetrahydrofuran (10 ml.) suspended in THF (10 ml.). After the reaction had subsided, cyclopentadienyl chromium dinitrosyl chloride (2.12g., 0.01 mole) in THF (100 ml.) was added. The colour of cyclopentadienyl chromium dinitrosyl chloride changed from greenish - yellow to brown - red, and the reaction mixture was filtered after stirring for 5 minutes. The solvent was evaporated, the residue dissolved in chloroform and chromatographed on neutral alumina.

On developing the column with petrol - ether (5:1), three bands separated. The upper two bands were the two isomers of di - μ - D_5 phenylthio - bis (cyclopentadienylnitrosyl - chromium) and mass spectrometry samples of each were prepared by crystallisation from methylene chloride and petrol yield (532 mg., 20.3%).

Preparation of Di - μ - D_5 phenylthio - bis (cyclopentadienyl carbonyl iron).

Thiophenol (0.46g., 0.004 mole) was converted into its sodium salt in THF (10 ml.) using 50% sodium hydride dispersion (0.2g., 0.005 mole). Cyclopentadienyl iron dicarbonyl bromide (1.03g., 0.004 mole) in THF (10 ml.) was added dropwise and the mixture stirred for 13 hours at room temperature. Evaporation of the solvent and heating the residue in refluxing benzene solution for 6 hours yielded di - μ - D_5 phenylthio - bis (cyclopentadienyl - carbonyl iron). (0.7g., 80%). Mass spectrometry samples were prepared by recrystallisation from petrol - ether solution.

Preparation of D_3 methyl mercaptan.

A mixture of D_3 methyl bromide (4 ml., 0.06 mole) and thiourea (4.5g., 0.075 mole) in 10 ml. water were

heated in a pressurebottle under a nitrogen atmosphere for 10 hours at 60°C. The bottle was cooled in solid carbon dioxide and the bottle opened. The thawed solution was then transferred to a three necked flask fitted with a nitrogen inlet, dropping funnel, condenser with a take off to a drying tube containing $CaSO_4$ and and thence to a liquid nitrogen cold trap.

Hydrolysis of the thiouronium bromide was effected by dropwise addition of 1M NaOH and heating the hydrolysed solution drove the liberated mercaptan into the cold trap. The cold trap was stoppered and removed from the apparatus, and allowed to warm up slowly. The evolved gas was allowed to bubble through a stirred suspension of sodium hydride in THF and the D_3 methyl mercaptan was thus isolated as the sodium salt.

Preparation of di μ - D_3 methylthio - bis (cyclopentadienyl nitrosyl chromium)

Cyclopentadienyl chromium dinitrosyl chloride (0.4g., 0.006 mole) in THF (50 ml.) was added to a stirred suspension of half the quantity of sodium mercaptide salt isolated as above, and the reaction stirred for 5 minutes. The solution was filtered and evaporated under vacuum and the residue chromatographed on neutral alumina. Purple crystals of di - μ - D_3

methylthio bis (cyclopentadienyl nitrosyl chromium) (70 mg., 19%) were obtained by recrystallisation from methylene chloride and petrol.

Preparation of μ-deuteroxo - μ methylthio - bis (cyclopentadienyl nitrosyl chromium.

1 mg of the mixed complex III was dissolved in 5 ml. dry THF, and stirred for 24 hours with a solution of potassium carbonate (10 mg.) in 5 ml. 99.7% D_2O. Separation and evaporation of the THF solution yielded a 90% isotopically pure sample of μ deuteroxo - μ methylthio - bis (cyclopentadienylnitrosyl chromium).

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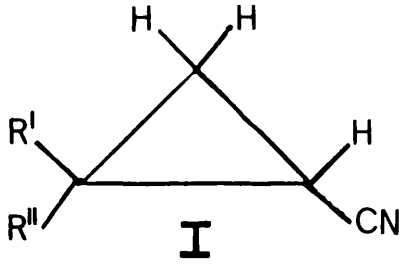
C H A P T E R 4

Studies of Rearrangement Ions in Organic Compounds



I

(a) $R^I = R^{II} = COOEt$

(b) $R^I = COOEt$, $R^{II} = COMe$

(c) $R^I = COOC(CH_3)_3$, $R^{II} = COMe$

(d) $R^I = R^{II} = COMe$

(e) $R^I = CN$, $R^{II} = COOMe$

(f) $R^I = CN$, $R^{II} = COOEt$

The Mass Spectra of Some Polyfunctional Cyclopropane Derivatives.

Mass Spectrometric studies of β keto - esters (1 - 3), diethyl malonates (4), and cyanoacetates (5) have recently been made. Skeletal rearrangement fragment ions have been observed in these compounds and in addition occur in α,β unsaturated esters (1), β diketones (6) and in other groups of compounds containing carbonyl functions (7 - 10). The importance of such fragments in the mass spectra of simple compounds is not only of importance in the understanding of fragmentation modes, but is also of obvious relevence in the construction of element maps (11) for automatic structural analysis.

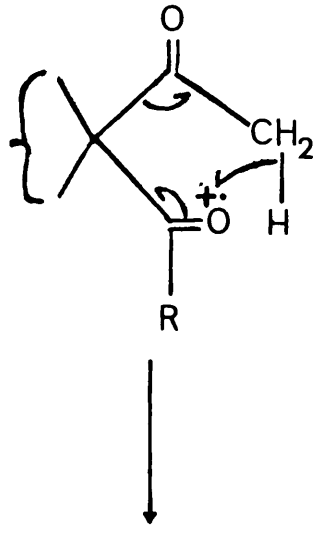
In order to investigate the possibility that similar rearrangements might occur in other related systems, a study of the compounds I(a - f) was undertaken. Tables of normalized spectra of these compounds are included at the rear of this chapter and Table 1 shows the precise mass measurements made to determine the nature of the fragmentation routes.

Table 1

Precise Mass Measurement of ions in the spectra of Cyclopropane Derivatives

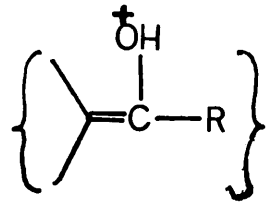
	m/e	Observed Mass	Formula	Theoretical
(a)				
	184	184.06042	$C_8H_{10}NO_4$	184.06092
	167	167.05372	$C_7{}^{13}CNO_3$	167.05377
	166	166.05071	$C_8H_8NO_3$	166.05041
	138	138.01894	$C_6H_4NO_3$	138.01911
	111	111.03202	$C_5H_5NO_2$	111.03202
	93	93.02132	C_5H_3NO	93.02146
	66	66.03442	C_4H_4N	66.03437
(b)				
	154*	154.05000	$C_7H_8NO_3$	154.05041
	154	154.06279	$C_8H_{10}O_3$	154.06298
	153	153.04268	$C_7H_7NO_3$	153.04258
	141	141.05481	$C_7H_9O_3$	141.05516
	136	136.03965	$C_7H_6NO_2$	136.03985
	111	As observed in (a)		
	113	113.02386	$C_5H_5O_3$	113.02386
(d)				
	136	As observed in (b)		

Scheme A



(b) R = OEt

(d) R = Me

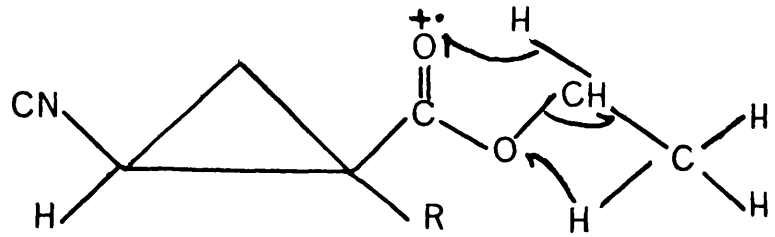


	m/e	Observed Mass	Formula	Theoretical
	124	124.05204	$C_7H_8O_2$	124.05240
	111	111.04480	$C_6H_7O_2$	111.04460
	109*	109.05252	C_6H_7O	109.05276
	109	109.02854	C_6H_5O	109.02895
	94	94.02906	C_5H_4NO	94.02920
(e)	123	123.03213	$C_6H_5O_2N$	123.03202
	105	105.04478	$C_6H_5N_2$	105.04520
	80	80.01363	C_4H_2NO	80.01363
	64	64.01841	C_4H_2N	64.01872
(f)	137	137.03558	$C_6H_5N_2O_2$	137.03509
	136	136.02734	$C_6H_4N_2O_2$	136.02721
	119	119.02491	$C_6H_3N_2O$	119.02453
	118	118.01645	$C_6H_2N_2O$	118.01671
	91	91.02981	$C_5H_3N_2$	91.02962

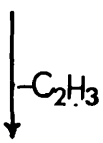
* Signifies the ion of greater abundance in the doublet.

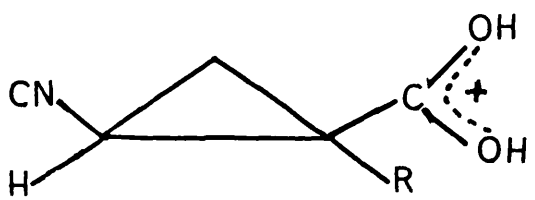
In the spectra of Ib and Id, loss of ketene from the molecular ion to form enolic fragment ions by the transfer of hydrogen from methyl by Scheme A is a major process as is the case in ethyl acetoacetate (7)

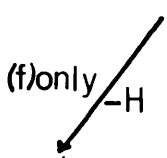
Scheme B



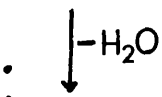
(a) R = COOEt
(b) R = COMe
(c) R = CN

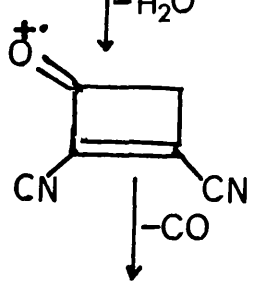






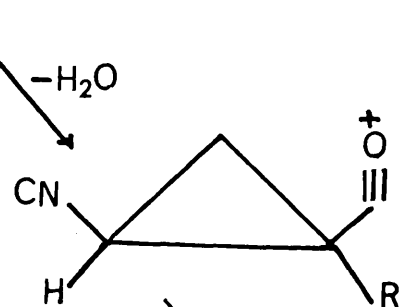
m/e 136



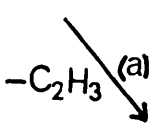


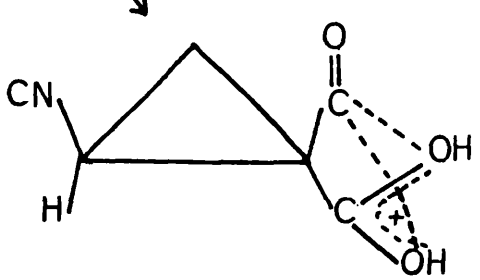
j

m/e 90



i





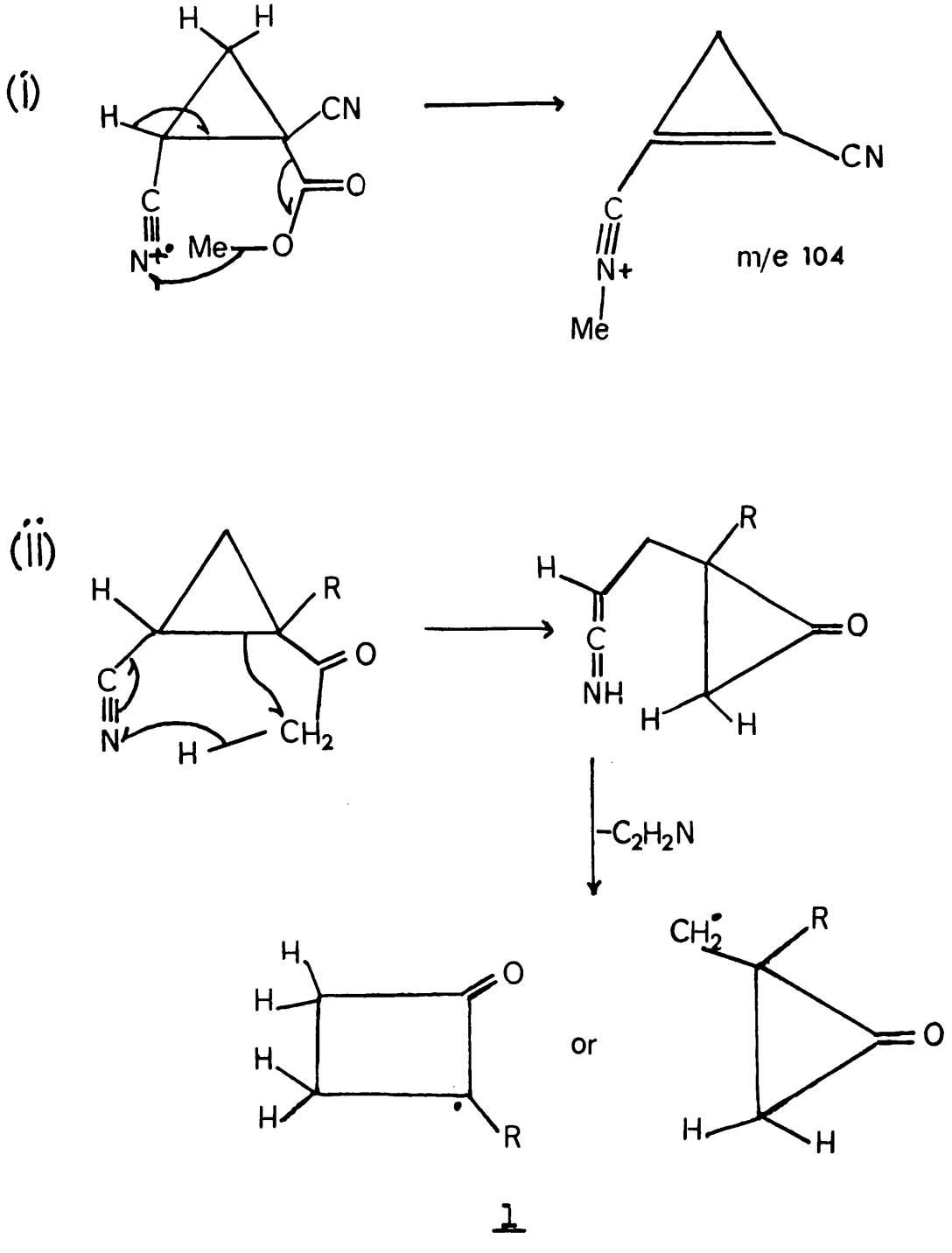
k

and acetyl acetone (6), whereas in Ic, the abundance of the corresponding ion is $< 2\%$ of the base peak. This is no doubt due to the fact that greater stabilization in Ic is attained by removal of a methyl group from the tertiary butyl centre to form an oxonium ion.

Elimination of 27 mass units occurs from the parent ion of I(a), (b), (d), (e) and (f), but only in those cases where there is no carboxyethyl group as in (d) and (e) does this correspond to the elimination of hydrogen cyanide. In all the other cases elimination of C_2H_3 with concomitant double hydrogen transfer to form an ion of structure h occurs, as per scheme B. Loss of water from h then follows in each case - a feature common to most esters greater than methyl. I(f), however, in addition to these decomposition processes demonstrates elimination of a hydrogen atom from h followed by elimination of water. The driving force for this mode of decomposition is regarded as being the formation of the highly conjugated di - cyano cyclobutenone system j which further decomposes by abstraction of carbon monoxide.

I(a) behaves in a like manner to diethyl malonate but differs in that loss of $C_2H_3^{\cdot}$ can also occur from the ion i to form k, which it is postulated may have

Scheme C


(i)
H
H
H
CN
C
N+
Me
O
O
CN
C
N+
Me
m/e 104
(ii)
H
R
C
N
H
CH2
O
H
R
C
NH
O
H
H
-C2H2N
H
H
H
H
O
R
or
CH2
R
O
H
H

1

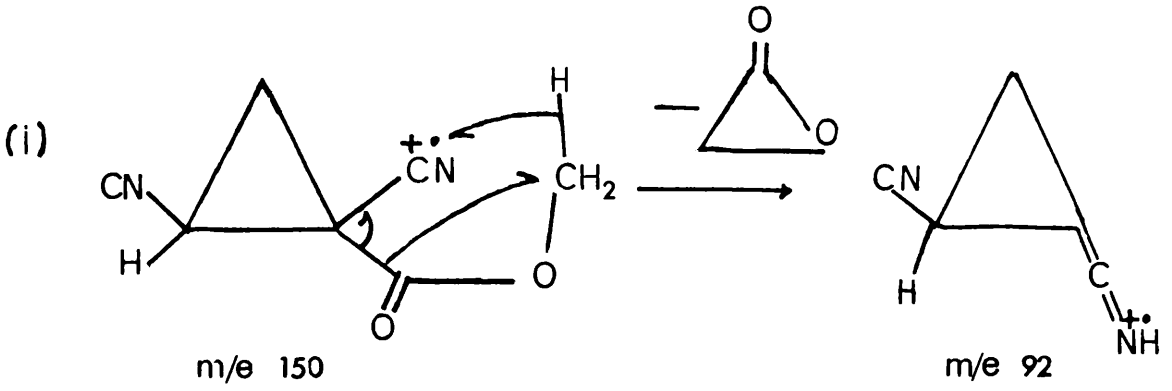
a non-classical oxonium ion structure. It is possible that the greater rigidity of the ring system permits such an ion form to exist, whereas in the corresponding aliphatic compound greater flexibility is allowed.

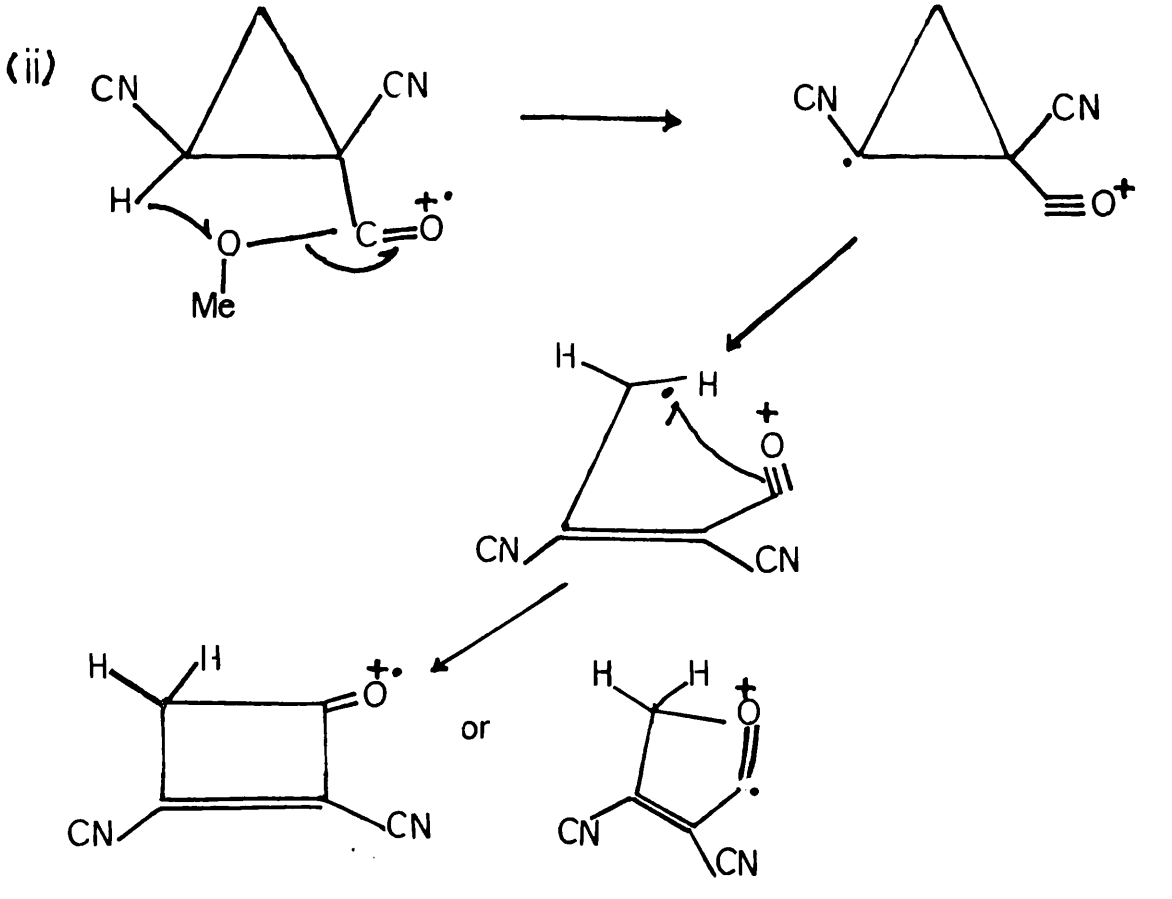
It was expected that the α- cyano esters I(e) and I(f) would show alkyl migrations similar to those observed in methyl and ethyl cyanoacetate (E). However, high resolution mass measurements have shown that only in I(e) is there an ion corresponding to $(P - HCO_2)^+$ as per scheme C. No such migration occurs in (f).

A rearrangement process, however, which had not been anticipated occurs in I(b), I(c) and I(d). All have acetyl groups β to cyano substituents and with no exceptions show removal of a fragment of 40 mass units from either the parent ion or a fragment ion, or both (as in I(b)). This corresponds to a formula C_2H_2N which is either CH_2CN or CH = C = NH. Either way, it involves hydrogen transfer from the methyl group of the acetyl residue with possibly simultaneous formation of a cyclobutanone system 1 as in Scheme C.

There is no doubt that the active group is the acetyl substituent as not only does the process <u>not</u> occur for substituents other than acetyl; but also evidence is

Scheme D


(i)
CN
H
+·CN
H
CH2
O
O
O
O
CN
H
C
+·NH
m/e 150
m/e 92


(ii)
CN
CN
H
O
Me
C
+·O
CN
CN
O+
H
H
+
O
CN
CN
H
H
+·O
CN
CN
or
H
H
+
O
CN
CN

present in the spectra that fragmentation of the other substituents occurs normally after the elimination and transfer have taken place. Thus in I(b) removal of C_2H_2N between m/e 181 and m/e 141 is closely followed by loss of C_2H_4 from the ethyl group of the ester.

Two further rearrangement mechanisms which take place only from the molecular ion of I(e) are worthy of mention. The first involves fragmentation with loss of $COOCH_2$ in the formation of m/e 92, and therefore involves hydrogen transfer from the methyl of the ester group. This is visualized as in Scheme D.

Additionally rearrangement can occur in the opposite manner by elimination of methanol from the parent ion. This is not a common rearrangement process in methyl esters and it is postulated that rearrangement occurs as in Scheme D, with formation of a highly conjugated dicyano cyclobutenone system. The origin of this ion is to be compared with the formation of _i_ scheme B, in the decomposition of the other dicyano substituted compound I(f).

Conclusions.

The mass spectra of the polyfunctional cyclopropane systems studied show features similar to related aliphatic species. Expected rearrangement ions involving

alkyl migrations, present in the spectra of related cyanoesters occur only in the methyl ester of the cyclopropane compounds which are α,β dicyano substituted, due to the more energetically favourable formation of a highly conjugated dicyano - cyclobutenone system.

In addition, however, rearrangement ions are observed in the cyclopropane systems with cyano groups β to acetyl substituents where hydrogen transfer and rearrangement are observed with elimination of C_2H_2N.

Experimental

All mass spectra were obtained on an A.E.I. MS9 double - focusing mass spectrometer at an ionizing voltage of 70eV. Samples were admitted through the hot inlet system at a temperature of 120°C and a source temperature of 150°C. Mass measurements were performed at a resolution of 10,000 on the 10% valley definition. Tables of mass spectra are shown overleaf.

The author would like to acknowledge the provision of samples by Drs. S.O. Lawesson and P. Madsen of the University of Aarhus, Denmark.

Mass Spectrum of I(a).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
29	100.0	93	30.2	153	2.6		
30	2.2	94	13.6	155	11.2		
38	8.2	95	4.0	156	2.9		
39	17.0	99	3.5	165	1.5		
40	2.5	100	0.9	166	50.5		
41	2.3	109	1.6	167	6.0		
42	3.0	110	2.5	184	30.1		
43	63.2	111	22.4	185	3.1		
44	6.0	112	5.2	211	7.4(P).		
45	5.3	113	2.5	212	1.4		
64	5.2	120	4.2				
65	15.5	121	4.2				
66	32.4	122	2.0				
67	4.2	127	2.4				
68	4.9	128	1.2				
69	14.3	135	1.4				
70	4.0	136	7.0				
82	2.7	137	11.2				
83	23.1	138	28.1				
84	6.0	139	4.0				
85	1.2	140	5.0				
92	0.5	141	3.2				

Mass Spectrum of I(b).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
43	100.0	84	4.5	142	2.0		
44	13.0	91	4.5	152	2.0		
45	4.0	93	42.8	153	21.0		
50	2.0	94	42.9	154	6.4		
51	3.0	95	3.5	166	8.0		
52	6.0	97	2.0	167	1.5		
53	6.0	107	3.0	181	6.0		
54	4.0	108	2.0	182	2,5		
55	4.0	109	9.6	183	1.0		
56	1.1	110	2.0	209	1.0(P).		
57	1.0	111	23.5				
58	3.5	113	11.5				
66	35.0	120	3.0				
67	5.0	122	2.0				
68	3.0	126	4.5				
69	3.0	135	10.0				
70	1.5	136	53.0				
79	3.0	137	7.0				
80	2.0	138	14.0				
81	4.0	139	8.0				
82	4.0	140	1.0				
83	14.0	141	16.0				

Mass Spectrum of I(c).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
43	100.0						
55	46.2						
56	94.0						
57	97.0						
66	99.0						
67	17.0						
94	99.0						
95	10.0						
96	1.0						
97	2.0						
109	76.0						
110	10.0						
111	3.9						
136	37.0						
137	3.5						
153	2.0						
154	14.5						
194	4.2						
195	1.0						
209	1.0(P).						

Mass Spectrum of I(d).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
43	100.0						
44	15.0						
58	10.5						
64	5.0						
65	4.5						
66	48.5						
67	4.0						
94	13.3						
109	28.2						
110	2.9						
111	3.5						
124	6.2						
136	35.0						
137	3.0						
151	23.2(P).						
152	2.0						

Mass Spectrum of I(e).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
27	10.5	63	17.0	121	4.0		
28	35.3	64	36.2	123	10.2		
29	16.8	65	14.1	124	1.7		
30	5.0	66	20.0	149	11. 0		
31	6.5	78	3.9	150	53.0(P).		
37	22.0	79	9.0	151	5.0		
38	20.4	80	27.4				
39	15.5	81	1.8				
40	65.0	89	2.6				
42	16.2	90	11.2				
43	14.0	91	57.3				
44	6.3	92	27.2				
50	2.3	93	9.9				
51	13.8	94	16.0				
52	37.5	95	2.3				
53	7.0	105	6.0				
54	7.9	106	0.2				
55	17.2	107	3.6				
57	2.0	108	3.9				
58	6.0	118	53.0				
59	100.0	119	51.2				
62	7 .5	120	6.1				

Mass Spectrum of I(f).

M/e	%Abund.	M/e	%Abund.	M/e	%Abund.	M/e	%Abund.
36	1.0	62	3.1	94	2.0		
37	9.0	63	8.5	95	1.0		
38	10.5	64	19.0	105	1.5		
39	8.0	65	16.9	106	1.5		
40	33.0	66	7.0	107	2.0		
41	16.9	67	4.5	108	6.5		
42	3.5	68	10.0	109	10.0		
43	10.5	69	2.0	111	1.5		
44	9.5	70	1.0	112	1.0		
45	8.2	71	1.5	118	26.0		
49	1.0	77	1.5	119	37.0		
50	1.5	78	1.5	120	7.5		
51	6.0	79	2.1	121	2.5		
52	23.0	80	11.5	123	3.0		
53	17.9	81	16.0	124	1.0		
54	10.9	82	1.5	136	60.0		
55	5.0	83	1.5	137	18.5		
56	3.0	89	2.0	138	2.0		
57	3.0	90	4.5	164	2.5(P).		
58	1.5	91	33.0	165	1.0		
59	21.0	92	20.0	166	1.5		
60	1.5	93	5.5				

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